

PROCESS FOR PREPARING ETHYLENE AND/OR PROPYLENE AND AN ISO-
OLEFIN-DEPLETED C4 OLEFINIC PRODUCT

Field of the invention

The invention relates to a process for preparing ethylene and/or propylene and an iso-olefin-depleted C4 olefinic product.

5 Background to the invention

Methanol-to-olefin processes are well described in the art. Typically, methanol-to-olefin processes are used to produce predominantly ethylene and propylene. An example of such a methanol-to-olefin process is described in
10 WO-A 2006/020083. In the process of WO-A 2006/020083, the methanol is first converted into dimethylether (DME) prior to be subjected to a conversion to olefins, thereby reducing the amount of water produced during the conversion to olefins. Both methanol and DME are suitable feedstocks
15 for a Methanol-to-olefin process and therefore such processes are also generally referred to as oxygenate-to-olefin (OTO) processes.

In EP2024303A1, another OTO process is described wherein in addition to oxygenates, also C4 olefins are
20 provided to the OTO process. These C4 olefins are provided as an olefinic co-feed together with the oxygenates. By providing a C4 olefinic co-feed to the OTO process more ethylene and propylene may be produced. According to EP2024303A1, suitable sources for these C4 olefins are for
25 instance C4 hydrocarbon fractions obtained from refinery units such as thermal cracking units, catalytic cracking units, steam cracking units, naphtha (steam) cracking units, butadiene extraction units, semi-hydrogenation units

for hydrogenation of C4 diolefins to predominantly C4 mono-olefins.

However, these C4 hydrocarbon fractions are a major resource for producing raffinate-2, which is a mixture of normal butenes and mixed butanes. Raffinate-2 is a chemical building block used in the manufacture of secondary butyl alcohol (SBA) and methyl ethyl ketone (MEK). SBA is an intermediate in the production of industrial cleaning compounds, oil treating chemicals and paint removers, and MEK is an intermediate in the production of surface coatings, adhesives, thinners, printing inks and cleaning agents. In addition, raffinate-2 is a valuable feedstock for olefin metathesis and alkylation processes. Further, butene-1 can be recovered from raff-2 through distillation. Butene-1 is a preferred co-monomer in the polyethylene synthesis.

By providing the mentioned C4 hydrocarbon fractions to an OTO process, less raffinate-2 is available, which may lead to a discrepancy between the raffinate-2 demand and supply.

Summary of the invention

There is a need in the art for a process, which would allow the provision of C4 olefins from the C4 hydrocarbon fractions obtained from refinery units to an OTO process, while maintaining the raffinate-2 supply.

It has now been found that it is possible to provide C4 olefins from the C4 hydrocarbon fractions obtained from refinery units to an OTO process and at the same time produce raffinate-2, by reacting iso-olefins in C4 hydrocarbon fraction with an alcohol into a tert-alkyl ether. The C4 iso-olefins are provided to an OTO process as

tert-alkyl ethers, while the iso-olefin-depleted C4 hydrocarbon fraction may be used as raffinate-2 for further purposes.

Accordingly, the present invention provides a process for preparing ethylene and/or propylene and an iso-olefin-depleted C4 olefinic product, comprising the steps of:

- a) providing a C4 hydrocarbon stream, comprising normal olefins and iso-olefins;
- b) subjecting the C4 hydrocarbon stream to an etherification process with methanol and/or ethanol wherein at least part of the iso-olefins are converted with methanol and/or ethanol to an tert-alkyl ether, and retrieving an etherification product stream;
- c) separating at least part of the etherification product stream into at least an ether-enriched stream and a first iso-olefin-depleted C4 olefinic product;
- d) converting at least part of the tert-alkyl ether in the ether-enriched stream to ethylene and/or propylene by contacting least part of the ether-enriched stream with a molecular sieve-comprising catalyst at a temperature in the range of from 350 to 1000 °C and retrieving a second olefinic product comprising ethylene and/or propylene.

By extracting iso-olefins from the C4 hydrocarbon stream as tert-alkyl ethers and providing the tert-alkyl ethers as a feed to an oxygenate-to-olefins process, ethylene and/or propylene may be produced. At the same time, the remaining C4 hydrocarbon stream, i.e. iso-olefin-depleted C4 olefinic product, is suitable for use as raffinate-2 and extraction of butene-1.

Brief description of the drawings

In Figure 1 a schematic representation is given of an embodiment of the process according to the invention.

In Figure 2 another schematic representation is given of an embodiment of the process according to the invention.

Detailed description of the invention

C4 olefins may suitably be used as part of the feed to an OTO process to produce ethylene and/or propylene. In the process according to the present invention part of the olefins in a C4 hydrocarbon stream, i.e. the iso-olefins, are extracted from the C4 hydrocarbon stream.

The iso-olefins are extracted by reacting the iso-olefins with an alcohol, in particular methanol and/or ethanol to form tert-alkyl ethers, such as for example methyl tert-butyl ether (MTBE) or ethyl tert-butyl ether (ETBE). The formed ethers can be separated from the remainder of the C4 hydrocarbon stream, i.e. the iso-olefin depleted olefinic product.

The tert-alkyl ethers, obtained by extracting the iso-olefins from the C4+ hydrocarbon fraction by reacting the iso-olefins with methanol and/or ethanol, are subsequently converted to at least further ethylene and/or propylene in an OTO process.

The remaining C4 hydrocarbon stream, i.e. iso-olefin-depleted C4 olefinic product, comprises predominantly normal butenes and preferably mixed butanes. This is a composition suitable to be used as raffinate-2, for instance to produce secondary butyl alcohol and methyl-ethyl ketone, alkylate or higher olefins through olefin metathesis or propylene through metathesis with ethylene and butene-1.

The process according to the invention is now described in more detail herein below.

The process according to the present invention is a process for preparing ethylene and/or propylene and an iso-olefin-depleted C4 olefinic product. In the process according to the invention, a C4 hydrocarbon stream, comprising normal olefins, i.e. 1-butene and/or 2-butene, and iso-olefins, i.e. isobutene, is provided. The C4 hydrocarbon stream may also comprise C4 paraffins, including normal butane and isobutane. The C4 paraffins are also referred to as mixed butanes. Preferably, the C4 hydrocarbon stream comprises in the range of from 60 to 100wt%, more preferably 80 to 100wt%, even more preferably 95 to 100wt%, still more preferably 97 to 100wt%, of C4 hydrocarbons, based on the total weight of the C4 hydrocarbon stream. Reference herein to C4 hydrocarbons is to hydrocarbons comprising four carbon atoms. Reference herein to hydrocarbons is to molecules comprising only carbon atoms and hydrogen atoms. Preferably, the C4 hydrocarbon stream comprises in the range of from 10 to 100wt% of olefins based on the weight of the C4 hydrocarbons in the C4 hydrocarbon stream, preferably of from 60 to 100wt% of C4 olefins based on the weight of the C4 hydrocarbons in the C4 hydrocarbon stream. Preferably, the C4 hydrocarbon stream comprises in the range of from 1 to 60wt% of iso-olefins based on the weight of the C4 olefins in the C4 hydrocarbon stream, preferably of from 10 to 50wt% of C4 iso-olefins based on the weight of the C4 olefins in the C4 hydrocarbon stream. Optionally, the C4 hydrocarbon stream also contains a diluent. Examples of suitable diluents include, but are not limited to, water or

steam, nitrogen, argon, C2-C3 paraffins and methane. One example of a suitable C4 hydrocarbon stream is the C4 cut of a FCC effluent stream, which typically contains 20wt% of isobutylene and a ratio of C4 olefins to C4 paraffins of 1.8.

In step (b) of the process according to the invention, the C4 hydrocarbon stream is subjected to an etherification process. In the etherification process, the C4 hydrocarbon stream is contacted with an alcohol, preferably methanol and/or ethanol, in the presence of a suitable etherification catalyst. When the iso-olefins, i.e. the isobutylenes, in the C4 hydrocarbon stream are contacted with the alcohol in the presence of an etherification catalyst, at least part of the iso-olefins are converted with the alcohol to tert-alkyl ethers. Reference herein in to a tert-alkyl ether is to an ether of an alcohol and an iso-olefin. Preferably, the alcohol is methanol and/or ethanol and the tert-alkyl ethers are methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE), which are tert-alkyl ethers of respectively methanol and ethanol with isobutene. From the etherification process, an etherification product stream is retrieved. The etherification product stream will comprise the formed tert-alkyl ethers and the remainder of the C4 hydrocarbon stream, i.e. the unreacted components, including normal butenes and optionally mixed butanes. In addition, the etherification product stream may also comprise unreacted alcohol.

At least part, and preferably all, of the etherification product stream is separated in step (c) into at least an ether-enriched stream and a first iso-olefin-

depleted C4 olefinic product, including normal butenes and optionally mixed butanes. The separation of the etherification product stream into an ether-enriched stream and an iso-olefin-depleted C4 olefinic product can be done with normal separation means provided in the art. Typically the etherification reaction is performed in the presence of an excess of alcohol, i.e. above reaction stoichiometry with the iso-olefin. Due to the relatively high boiling points of methanol and ethanol, the bulk of the excess alcohol can be directed toward the ether-enriched stream. Methanol may form an azeotropic mixture with the C4 normal olefins in the iso-olefin-depleted C4 hydrocarbon stream. The methanol concentration in the azeotropic mixture is approximately 4wt%, based on weight of the azeotropic mixture. The ethanol may also form an azeotropic mixture with the butenes, wherein the ethanol concentration in the azeotropic mixture is approximately 2wt%, based on weight of the azeotropic mixture. In the case of etherification with a mixed methanol/ethanol stream to produce MTBE and ETBE, there are two different azeotropes. It may be desired to remove the alcohol prior to providing the iso-olefin-depleted C4 olefinic product as feedstock to another process. Alcohols are for instance an undesired component in a feed stream to an alkylation unit. In addition, methanol and ethanol are a valuable feedstock for producing ethylene and propylene and is therefore preferably captured. Alcohol may be extracted from the iso-olefin-depleted C4 olefinic product by a water extraction. In one embodiment, alcohols are separated from hydrocarbons in an extraction column. Alcohols and hydrocarbons are fed to the bottom part of the extractor and water to the top section.

The column is typically filled with random packing or sieve trays, which enhance alcohol mass-transfer from the hydrocarbon phase to the water phase. Essentially alcohol-free hydrocarbons may be retrieved above the water feed point, and a water/alcohol mixture is the bottom product. The alcohol may separated from the water by distillation and led back to the etherification process, or preferably the water/alcohol mixture may be contacted with a molecular sieve to produce ethylene and/or propylene, for instance by providing the water/alcohol mixture to an OTO unit.

The iso-olefin-depleted C4+ olefinic product may be exported from the process and used as raffinate-2. If desired the iso-olefin-depleted C4+ olefinic product may be provided to step (d) of the process as a co-feed. This may be of interest in case of a temporary decreased external raffinate-2 demand. In the latter case it is not necessary to separate the azeotropic alcohol from the iso-olefin-depleted C4+ olefinic product, instead the azeotrope can be provided as such, without removal of the alcohol.

In the process according to the present invention, ethylene and/or propylene are produced in step (d) by converting at least part of the tert-alkyl ethers in the ether-enriched stream to ethylene and/or propylene. At least part of the tert-alkyl ethers in the ether-enriched stream are converted by providing at least part of the ether-enriched stream to a reactor and contacting at least part of the ether-enriched stream with a molecular sieve-comprising catalyst to obtain a second olefinic product, comprising ethylene and/or propylene. In addition, the second olefinic product may also comprise C4 olefins as part of a C4+ hydrocarbon fraction in the second olefinic

product. An advantage of the present invention is that the C4+ hydrocarbon fraction in the second olefinic product comprises relatively low concentration of paraffins due to the low concentration, if any, of paraffins in ether-enriched stream. The low concentration of paraffins in this fraction makes it particularly suitable for use as raffinate-2.

The ether-enriched stream is contacted with the molecular sieve-comprising catalyst at a temperature in the range of from 350 to 1000 °C, preferably of from 350 to 750 °C. When the tert-alkyl ethers, and in particular MTBE and/or ETBE, are contacted with molecular sieves, i.e. the molecular sieve in the molecular sieve-comprising catalyst, the tert-alkyl ethers are at least partially converted to at least ethylene and/or propylene, preferably ethylene and propylene. In addition to ethylene and/or propylene, also C4 olefins may be formed. As the tert-alkyl ethers are oxygenates, the conversion of the tert-alkyl ethers in the ether-enriched stream may be considered as an OTO process and operated as such an OTO process. Process conditions for operating an OTO process are provided herein below.

In a preferred embodiment of step (d), step (d) comprises contacting an oxygenate-comprising feedstock with the molecular sieve-catalyst and wherein the oxygenate-comprising feedstock comprises tert-alkyl ether obtained in step (b) and one or more other oxygenates, preferably at least one of methanol and dimethylether, more preferably methanol. Methanol is preferred in particular when the alcohol used to form the ether is also methanol.

The conversion of oxygenates such as methanol and DME, under such conditions, to olefins in the presence of

molecular sieve-comprising catalysts is well known in the art. With respect to the tert-alkyl ethers it is believed, without wishing to be bound to a particular theory, that upon contacting the molecular sieve-catalyst, the tert-alkyl ether decomposes into its corresponding alcohol, i.e. methanol and/or ethanol, and iso-olefin, i.e. isobutene. This decomposition reaction is acid-catalysed. Therefore, preferably the molecular sieve-comprising catalyst comprises acid groups. Some molecular sieves are acidic by nature, whereas other molecular sieve-comprising catalysts comprise binder, support, matrix or other materials comprising acid groups. Even theoretically non-acidic molecular sieves typically comprise some residual acid groups introduced during preparation of the molecular sieve and/or molecular sieve-comprising catalyst. In the absence of any acid groups in the molecular sieve-comprising catalyst it may be preferred to add such groups either by treating the molecular sieve-comprising catalyst to introduce such groups essentially at the surface of the catalyst through impregnation with an acid that resides on the catalyst after calcination, for instance by treating the molecular sieve-comprising catalyst with an acid, such as phosphoric acid, or adding an acid component to catalyst formulation comprising the molecular sieve-comprising catalyst, such as alumina.

Alternatively, the oxygenate-comprising feedstock is contacted with an acid catalyst, prior to contacting the molecular sieve-comprising catalyst. This may for instance be done by passing oxygenate-comprising feedstock through an acid catalyst comprising bed or by passing the feedstock through an acid grid or filter. Preferably, the oxygenate-

comprising feedstock is contacted with the acid catalyst at a temperature above 150°C. More preferably, the oxygenate-comprising feedstock is contacted with the acid catalyst at a temperature above 350°C.

5 Preferably, steam is present as the tert-alkyl ether contacts the catalyst. Steam is believed to increase the selectivity of the reaction.

10 At least part of the alcohol, preferably methanol and/or ethanol, obtained following the decomposition of the tert-alkyl ether is subsequently converted to ethylene and/or propylene over the molecular sieve-comprising catalyst under the process conditions applied. Any residual methanol in the ether-enriched stream is also converted under these conditions.

15 As mentioned hereinabove it is believed that upon contact with the molecular sieve-comprising catalyst, the tert-alkyl ether decomposes into an alcohol and an isobutene. Depending on the nature of the molecular sieve in the molecular sieve-comprising catalyst, the obtained isobutene is either, at least partially, converted to ethylene and/or propylene or remains unconverted.

20 Any isobutene which is not converted in step (d) is retrieved from the process as part of the second olefinic product. In addition to any unconverted isobutene, the second olefinic product may also comprise C4 olefins as part of a C4+ hydrocarbon fraction produced as by-product in the conversion of oxygenates to ethylene and/or propylene. Preferably, the C4 olefins in the second olefinic product are at least partially converted by contacting, at least part of, the C4 olefins with a zeolite-comprising catalyst in a further step (e).

25

30

As mentioned herein above, the second olefinic product may comprise C4 olefins as part of a C4 hydrocarbon fraction of the second olefinic product. Part, or all, of this C4 hydrocarbon fraction may be provided together with or as part of the C4 hydrocarbon stream of step (a) to the etherification process of step (b). An advantage of providing part of this C4 hydrocarbon fraction to step (b) of the process is that additional raffinate-2 may be produced, as the C4 hydrocarbon fraction comprises isobutene, normal butene and mixed butanes. Typically, the C4 hydrocarbon fraction will comprise little to no butadiene. In case step (e) comprises that the C4 hydrocarbon fraction is provided to the etherification process of step (b), the catalyst in catalyst in step (d) will be a zeolite-comprising catalyst. Alternatively, the C4 hydrocarbon fraction may be provided directly to step (d).

The C4 olefins in the second olefinic product may also be converted in a separate unit, reactor or reactor zone downstream of the OTO unit. This is particularly preferred where molecular sieve-comprising catalyst in step (d) comprises at least one SAPO, AlPO, or MeAlPO type molecular sieve, preferably SAPO-34. These catalysts are less suitable for converting iso-olefins. Preferably, the C4 olefins are contacted with the zeolite-comprising catalyst at a reaction temperature of 350 to 1000 °C, preferably from 350 to 750 °C, more preferably 450 to 700°C, even more preferably 500 to 650°C; and a pressure from 0.1 kPa (1 mbar) to 5 MPa (50 bar), preferably from 100 kPa (1 bar) to 1.5 MPa (15 bar). Optionally, the stream comprising C4 olefins also contains a diluent. Examples of suitable

diluents include, but are not limited to, water or steam, nitrogen, argon and methane. Under these conditions, at least part of the C4 olefins are converted to a further olefinic product, comprising ethylene and/or propylene. The further olefinic product may be combined with the olefinic product obtained in step (d). Such a separate process step directed at converting C4 olefins to ethylene and propylene is also referred to as an olefin cracking process (OCP).

This further olefinic product may also comprise a C4 hydrocarbon fraction. The C4 hydrocarbon fraction of the further olefinic product may be recycled to either step (d) and/or step (e). Part, or all, of this C4 hydrocarbon fraction of the further olefinic product may also be provided to the etherification process of step (b) to produce additional raffinate-2.

In the process according to the invention, the C4 hydrocarbon stream may be any C4 hydrocarbon stream. The C4 hydrocarbon stream is typically an external stream. Examples of such streams are the C4 fraction of the effluent of a refinery unit such as thermal cracking units, catalytic cracking units, steam cracking units, naphtha (steam) cracking units, butadiene extraction units and semi-hydrogenation units for removal of C4 diolefins. A particularly preferred C4 hydrocarbon stream is raffinate-1. Reference herein to raffinate-1 is to a stream comprising of isobutenes, normal butenes and mixed butanes and essentially no butadienes. Reference herein to essentially no butadienes is to a butadiene content of in the range of from 0 to 0.5wt%, preferably 0 to 0.1, more preferably, 0 to 0.01 wt% of butadienes, based on the weight of the C4 hydrocarbons in the raffinate-1.

In the process according to the invention iso-olefins are reacted with methanol in an etherification process. The etherification process may be any suitable etherification process available in the art for etherifying methanol and iso-olefins to tert-alkyl ethers. Reference is made to the Handbook of MTBE and Other Gasoline Oxygenates, H. Hamid and M.A. Ali ed., 1st edition, Marcel Dekker, New York, 2004, pages 65 to 223, where several established process and catalyst for preparing tert-alkyl ethers such as MTBE and ETBE are described. In particular reference is made to chapter 9, pages 203 to 220 of the Handbook of MTBE and Other Gasoline Oxygenates, wherein suitable commercial etherification processes are described. A preferred etherification process is an etherification process wherein the iso-olefins are converted with methanol to a tert-alkyl ether in the presence of a catalyst. Any homogeneous or heterogeneous Brönsted acid may be used to catalyze the etherification reaction. Such catalyst include: sulfuric acid, zeolites, pillared silicates, supported fluorocarbonsulphonic acid polymers and protonated cation-exchange resins catalyst, preferred catalyst are protonated cation-exchange resins catalyst due to the higher catalytic activity and the bound acid sites. A commonly used catalyst is Amberlyst 15.

Preferably, the iso-olefins are converted with an alcohol, preferably methanol and/or ethanol, more preferably methanol, to a tert-alkyl ether at a temperature in the range of from 30 to 100°C, more preferably 40 to 80°C. Preferably, the iso-olefins are converted with methanol and/or ethanol to a tert-alkyl ether at a

pressures in the range of from 5 to 25 bar, more preferably 6 to 20 bar.

The iso-olefins may be converted with methanol and/or ethanol to a tert-alkyl ether in any etherification process, however, one preferred etherification process is based on a reactive distillation, which allows for a continuous etherification and separation of the formed ethers.

The C4 hydrocarbon stream can comprise diolefins. Preferably, the C4 hydrocarbon stream comprises in the range of from 0 to 0.5wt%, preferably 0 to 0.1, more preferably, 0 to 0.01 wt% of butadienes, based on the weight of the C4 hydrocarbons in the C4 hydrocarbon stream. Most preferably, the C4 hydrocarbon stream does not contain butadiene. Butadienes react to form undesired higher hydrocarbon compounds.

Preferably, the part of the C4 hydrocarbon stream subjected to the etherification process is selectively hydrogenated to remove at least part of any diolefins, by hydrogenating the diolefins to mono-olefins and/or paraffins, preferably to mono-olefins.

In the present invention, in step (d) an oxygenate-comprising feedstock is converted in an oxygenate-to-olefins process, in which an oxygenate feedstock is contacted in an OTO zone with an oxygenate conversion catalyst under oxygenate conversion conditions, to obtain a conversion effluent comprising ethylene and/or propylene. Reference herein to an oxygenate feedstock is to an oxygenate-comprising feedstock, including any feedstock comprising at least part of the tert-alkyl ether produced in step (b). An example of such an oxygenate-comprising

feedstock is a feedstock comprising at least part of the ether-enriched stream obtained in step (c). In the OTO zone, at least part of the feedstock is converted into an olefinic product, i.e. a product containing one or more olefins, including ethylene and/or propylene.

The oxygenate-comprising feedstock comprises at least one tert-alkyl ether, preferably selected from the group of methyl tert-butyl ether (MTBE) or ethyl tert-butyl ether (ETBE). Other tert-alkyl ethers may be comprised in the feedstock, such as tert-alkyl ethers obtained by the reaction between a C3+ alkyl alcohol and isobutene. Further oxygenates used in step (d) the process according to the invention may preferably be oxygenates, which comprise at least one oxygen-bonded alkyl group. The alkyl group preferably is a C1-C5 alkyl group, more preferably C1-C4 alkyl group, i.e. comprises 1 to 5, respectively, 4 carbon atoms; more preferably the alkyl group comprises 1 or 2 carbon atoms and most preferably one carbon atom. Examples of oxygenates that can be used in the oxygenate-comprising feedstock include alcohols and ethers. Examples of preferred oxygenates include alcohols, such as methanol, ethanol, propanol; and dialkyl ethers, such as dimethylether, diethylether, methylethylether. Preferably, the further oxygenate is methanol or dimethylether, or a mixture thereof.

Preferably the oxygenate-comprising feedstock comprises at least 50 wt% of oxygenate, based on the total of hydrocarbons and oxygenates in the oxygenate-comprising feedstock, more preferably at least 70 wt%.

The oxygenate feedstock can comprise an amount of diluents. During the conversion of the oxygenates, steam is

produced as a by-product, which serves as an in-situ produced diluent. Optionally additional steam is added as diluent. The amount of additional diluent that needs to be added depends on the in-situ water make, which in turn depends on the composition of the oxygenate-comprising feed. Where methanol produces 1 mol of water per mol of carbon atoms supplied to the process, MTBE, for example only produces 0.20 mol of water per 1 mol of carbon atoms supplied to the process. Where the diluent is water or steam, the molar ratio of oxygenate to diluent is between 10:1 and 1:20. In case, the oxygenate-comprising feedstock comprises in the range of from 0.01 to 50 wt%, preferably of from 1 to 10wt%, of tert-alkyl ether, based on the oxygenates in the oxygenate-comprising feedstock, the molar ratio of oxygenate to diluent is preferably in the range of from 3:1 to 1:5, preferably 2:1 to 1:2. In case, the oxygenate-comprising feedstock comprises in the range of from 50 to 100wt%, preferably 60 to 95wt%, of tert-alkyl ether, based on the oxygenates in the oxygenate-comprising feedstock, the molar ratio of oxygenate to diluent is preferably in the range of from 1:3 to 1:15, preferably 1:4 to 1:10.

Due to the low in-situ water make of tert-alkyl ethers, the use of diluents other than water may be preferred, in particular when the catalyst is sensitive to hydrothermal deactivation. Other suitable diluents include inert gases such as nitrogen and methane, but may also include C2-C3 paraffins.

Preferably, in addition to the oxygenate, an olefinic co-feed is provided along with and/or as part of the oxygenate feedstock. Reference herein to an olefinic co-

feed is to an olefin-comprising co-feed. The olefinic co-feed preferably comprises C4 and higher olefins, more preferably C4 and C5 olefins. Preferably, the olefinic co-feed comprises at least 25 wt%, more preferably at least 50 wt%, of C4 olefins, and at least a total of 70 wt% of C4 hydrocarbon, based on weight of the olefinic co-feed.

Preferably, at least 70 wt% of the olefinic co-feed, during normal operation, is formed by a recycle stream of a C4+ hydrocarbon fraction from the OTO conversion effluent, preferably at least 90 wt% of olefinic co-feed, based on the whole olefinic co-feed, is formed by such recycle stream. In order to maximize production of ethylene and propylene, it is desirable to maximize the recycle of C4 olefins in the effluent of the OTO process. As described herein above, this can be done by recycling at least part of the C4+ hydrocarbon fraction, preferably a C4-C5 hydrocarbon fraction, more preferably C4 hydrocarbon fraction, in the olefinic product, which is retrieved as the OTO effluent. However, a certain part thereof, such as between 1 and 5 wt%, needs to be withdrawn as purge, since otherwise saturated hydrocarbons, in particular C4 saturated hydrocarbons (butane) would build up in the process, which are substantially not converted under the OTO reaction conditions.

The preferred molar ratio of oxygenate in the oxygenate feedstock to olefin in the olefinic co-feed provided to the OTO conversion zone depends on the specific oxygenate used and the number of reactive oxygen-bonded alkyl groups therein. Preferably the molar ratio of oxygenate to olefin in the total feed, i.e. oxygenate feed and olefinic co-feed, lies in the range of 20:1 to 1:10, more preferably in

the range of 18:1 to 1:5, still more preferably in the range of 15:1 to 1:3, even still more preferably in the range of 12:1 to 1:3.

5 A further advantage of using the selected tert-alkyl ethers as part of the oxygenate-comprising feedstock is that these ethers provide both an oxygenate, being methanol or ethanol, and an olefin, being isobutene, to the process in the form of a single molecule, which decomposes when contacted with the catalyst. This has the advantage that
10 both reactants, i.e. an oxygenate and an olefin, may be provided in a single feed component. For purposes of calculating the molar ratio of oxygenate to olefin in the total feed, the olefins provided to the process as part of the tert-alkyl ether must also be taken into account.

15 A variety of OTO processes is known for converting oxygenates to an olefin-containing product, as already referred to above. One such process is described in WO-A 2006/020083. Processes integrating the production of oxygenates from synthesis gas and their conversion to light
20 olefins are described in US20070203380A1 and US20070155999A1.

Catalysts suitable for converting the oxygenate-comprising feedstock preferably include molecular sieve-comprising catalyst compositions. Such molecular sieve-comprising catalyst compositions typically also include
25 binder materials, matrix material and optionally fillers. Suitable matrix materials include clays, such as kaolin. Suitable binder materials include silica, alumina, silica-alumina, titania and zirconia, wherein silica is preferred
30 due to its low acidity.

Molecular sieves preferably have a molecular framework of one, preferably two or more corner-sharing [TO₄] tetrahedral units, more preferably, two or more [SiO₄], [AlO₄] and/or [PO₄] tetrahedral units. These silicon, aluminum and/or phosphorous based molecular sieves and metal containing silicon, aluminum and/or phosphorous based molecular sieves have been described in detail in numerous publications including for example, U.S. Pat. No. 4,567,029. In a preferred embodiment, the molecular sieves have 8-, 10- or 12-ring structures and an average pore size in the range of from about 3 Å to 15 Å.

Suitable molecular sieves are silicoaluminophosphates (SAPO), such as SAPO-17, -18, -34, -35, -44, but also SAPO-5, -8, -11, -20, -31, -36, -37, -40, -41, -42, -47 and -56; aluminophosphates (AlPO) and metal substituted (silico)aluminophosphates (MeAlPO), wherein the Me in MeAlPO refers to a substituted metal atom, including metal selected from one of Group IA, IIA, IB, IIIB, IVB, VB, VIB, VIIIB, VIIIIB and Lanthanide's of the Periodic Table of Elements, preferably Me is selected from one of the group consisting of Co, Cr, Cu, Fe, Ga, Ge, Mg, Mn, Ni, Sn, Ti, Zn and Zr.

Alternatively, the conversion of the oxygenate feedstock may be accomplished by the use of an aluminosilicate-comprising catalyst, in particular a zeolite-comprising catalyst. Suitable 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.

Aluminosilicate-comprising catalysts, and in particular zeolite-comprising catalysts, have the additional advantage that in addition to the conversion of methanol or ethanol, these catalysts also induce the conversion of olefins to ethylene and/or propylene. As a result, at least part of the olefins obtained as the tert-alkyl ether is decomposed into methanol or ethanol and the corresponding iso-olefin, may also be converted into ethylene and/or propylene. Furthermore, these aluminosilicate-comprising catalysts, and in particular zeolite-comprising catalysts, are particularly suitable for use as the catalyst in an OCP. Particular preferred catalyst for the OCP reaction, i.e. converting part of the olefins in the second olefinic product, are catalysts comprising 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.

In one preferred embodiment, the molecular sieve in the molecular sieve-comprising catalyst of step (d) is a non-zeolitic molecular sieve, while part of the olefinic product retrieved in step (d), in particular at least part of the C4+ fraction containing olefins, is provided to a subsequent separate OCP unit with a zeolite-comprising catalyst and the C4+ hydrocarbon fraction is at least partially converted by contact with the zeolite-comprising catalyst in a step (e).

Preferred catalysts, for both the OTO reaction in step (d) as well as an optional OCP reaction in step (e), comprise a more-dimensional zeolite, in particular of the

MFI type, more in particular ZSM-5, or of the MEL type, such as zeolite ZSM-11. Such zeolites are particularly suitable for converting olefins, including iso-olefins, to ethylene and/or propylene. The zeolite having more-
5 dimensional channels has intersecting channels in at least two directions. So, for example, the channel structure is formed of substantially parallel channels in a first direction, and substantially parallel channels in a second direction, wherein channels in the first and second
10 directions intersect. Intersections with a further channel type are also possible. Preferably the channels in at least one of the directions are 10-membered ring channels. A preferred MFI-type zeolite has a Silica-to-Alumina ratio SAR of at least 60, preferably at least 80. The oxygenate
15 conversion catalyst can comprise at least 1 wt%, based on total molecular sieve in the oxygenate conversion catalyst, of the molecular sieve having more-dimensional channels, preferably at least 5 wt%, more preferably at least 8 wt%.

Particular preferred catalysts, for both the OTO
20 reaction in step (d) as well as an optional OCP reaction in step (e), include catalysts comprising one or more zeolite having one-dimensional 10-membered ring channels, i.e. one-dimensional 10-membered ring channels, which are not intersected by other channels. Preferred examples are
25 zeolites of the MTT and/or TON type. Preferably, the catalyst comprises at least 40wt%, preferably at least 50wt% of such zeolites based on total zeolites in the catalyst.

In a particularly preferred embodiment the catalyst,
30 for both the OTO reaction in step (d) as well as an optional OCP reaction in step (e), comprises in addition to

one or more one-dimensional zeolites having 10-membered ring channels, such as of the MTT and/or TON type, a more-dimensional zeolite, in particular of the MFI type, more in particular ZSM-5, or of the MEL type, such as zeolite ZSM-11.

The catalyst, for both the OTO reaction in step (d) as well as an optional OCP reaction in step (e), may comprise phosphorous as such or in a compound, i.e. phosphorous other than any phosphorous included in the framework of the molecular sieve. It is preferred that an MEL or MFI-type zeolites comprising catalyst additionally comprises phosphorous. The phosphorous may be introduced by pre-treating the MEL or MFI-type zeolites prior to formulating the catalyst and/or by post-treating the formulated catalyst comprising the MEL or MFI-type zeolites. Preferably, the catalyst comprising MEL or MFI-type zeolites comprises phosphorous as such or in a compound in an elemental amount of from 0.05 to 10 wt% based on the weight of the formulated catalyst. A particularly preferred catalyst comprises phosphor-treated MEL or MFI-type zeolites having SAR of in the range of from 60 to 150, more preferably of from 80 to 100. An even more particularly preferred catalyst comprises phosphor-treated ZSM-5 having SAR of in the range of from 60 to 150, more preferably of from 80 to 100.

It is preferred that molecular sieves in the hydrogen form are used in the oxygenate conversion catalyst in step (d), e.g., HZSM-22, HZSM-23, and HZSM-48, HZSM-5. Preferably at least 50wt%, more preferably at least 90wt%, still more preferably at least 95wt% and most preferably 100wt% of the total amount of molecular sieve used is in

the hydrogen form. It is well known in the art how to produce such molecular sieves in the hydrogen form.

The reaction conditions of the oxygenate conversion in step (d) include a reaction temperature of 350 to 1000 °C, preferably from 350 to 750 °C, more preferably 450 to 700°C, even more preferably 500 to 650°C; and a pressure from 0.1 kPa (1 mbar) to 5 MPa (50 bar), preferably from 100 kPa (1 bar) to 1.5 MPa (15 bar).

Typically the catalyst deactivates in the course of the process, primarily due to deposition of coke on the catalyst. Conventional catalyst regeneration techniques can be employed to remove the coke. It is not necessary to remove all the coke from the catalyst as it is believed that a small amount of residual coke may enhance the catalyst performance and additionally, it is believed that complete removal of the coke may also lead to degradation of the molecular sieve. This applies to both the catalyst used in step (d) of the process as well as the catalyst in the optional step (e) of the process.

The catalyst particles used in the process of the present invention can have any shape known to the skilled person to be suitable for this purpose, for it can be present in the form of spray dried catalyst particles, spheres, tablets, rings, extrudates, etc. Extruded catalysts can be applied in various shapes, such as, cylinders and trilobes. If desired, spent oxygenate conversion catalyst can be regenerated and recycled to the process of the invention. Spray-dried particles allowing use in a fluidized bed or riser reactor system are preferred. Spherical particles are normally obtained by

spray drying. Preferably the average particle size is in the range of 1 - 200 μm , preferably 50 - 100 μm .

Both the OTO process of step (d) as the optional OCP process of step (e) may be operated in a fluidized bed or moving bed, e.g. a fast fluidized bed or a riser reactor system, and also in a fixed bed reactor or a tubular reactor. A fluidized bed or moving bed, e.g. a fast fluidized bed or a riser reactor system are preferred.

In step (d) of the process a second olefinic product stream comprising ethylene and/or propylene is retrieved. As described herein above, in step (e) a further olefinic product stream comprising ethylene/and propylene may be obtained. The ethylene and/or propylene may be separated from the remainder of the components in the olefinic products. Preferably the olefinic product and further olefinic product at least partially, and preferably fully, combined prior to separating the ethylene and/or propylene from the remaining components. Where the olefinic product comprises ethylene, least part of the ethylene may be further converted into at least one of polyethylene, mono-ethylene-glycol, ethylbenzene and styrene monomer. Where the olefinic product comprises propylene, at least part of the propylene may be further converted into at least one of polypropylene and propylene oxide.

In the process according to the invention at least part of tert-alkyl ethers are converted to ethylene and/or propylene. Optionally, another part of the tert-alkyl ethers are exported from the process as products, e.g. MTBE. Such ethers are suitably used as fuel additives.

Detailed description of the drawings

In Figure 1, a process according to the present invention is schematically represented. In Figure 1, C4 hydrocarbon stream 1 comprising C4 normal-olefins and iso-olefins is provided to etherification zone 5, together with methanol 10. In etherification zone 5, C4 hydrocarbon stream 1 is contacted with methanol 10 over an etherification catalyst, such as for instance a protonated cationic-exchange resin. Etherification product 15 is retrieved from etherification zone 5 and provided to separation zone 20, wherein etherification product 15 is separated into an ether-enriched stream 25 and an iso-olefin-depleted olefinic product 30. Optionally, zones 5 and 20 are combined into a reactive distillation zone, wherein iso-olefins are reacted with methanol to tert-alkyl ethers, while continuously separating tert-alkyl ether from the reaction mixture. Optionally, zones 5 and 20 allow for the recycle of part of the iso-olefin depleted stream in case not all of the iso-olefins are converted to tert-alkyl ether in a single pass process.

Iso-olefin-depleted olefinic product 30 is withdrawn from process and may be used as raffinate 2. Ether-enriched stream 25 is provided to oxygenate-to-olefin zone 35. In oxygenate-to-olefin zone 35, ether-enriched stream 25 is contacted with a molecular sieve-comprising catalyst, for example a catalyst comprising ZSM-5, such as a catalyst comprising 50wt% of ZSM-5 and 50wt% ZSM-23, based on the zeolite content in the catalyst, or a catalyst comprising SAPO-34. Optionally, additional oxygenate, such as methanol or dimethylether, olefins and water are added to oxygenate-to-olefin zone 35 (not shown). Second olefinic product 40, comprising ethylene and/or propylene is retrieved from

oxygenate-to-olefin zone 35. Preferably, second olefinic product 40 is further treated to separate the ethylene and/or propylene from the remainder of second olefinic product 40. Therefore, preferably second olefinic product 40 is provided to second separation zone 45. Second separation zone 45 may for instance include a quench tower set for receiving olefinic product 40. In the quench tower high boiling components such as water may be removed, the remaining stream may be compressed in a multi stage compressor zone, with interstage cooling and separation of condensed phases. The compressed vapour stream may be provided to a combination of a de-ethaniser and a de-propaniser to separate the compressed vapour stream into at least ethylene and/or propylene and a C4+ hydrocarbon fraction, comprising C4 olefins. The ethylene and/or propylene may be retrieved from second separation zone 45 separately or as a mixture via one or more streams 50. C4 olefins may be retrieved as part of stream 55. Stream 55 may also contain higher hydrocarbons, i.e. C5+ olefins and C4+ paraffins, however preferably any C5+ hydrocarbons are separated in second separation section 45 from the C4 hydrocarbons and retrieved as a separate C5+ hydrocarbon stream (not shown). C4 olefins in the second olefinic product, and optionally at least a part of the C5+ olefins in the second olefinic product, may be recycled back to OTO zone 35 (not shown) or to etherification zone 5 (not shown). Alternatively, for instance in case a non-zeolite catalyst such as SAPO-34 is used in OTO zone 35, at least part of the C4 olefins in the second olefinic product, and optionally at least a part of the C5+ olefins in the second olefinic product, are provided to reactor zone 60, which is

operated as an Olefin Cracking Process (OCP). In reactor zone 60, stream 55 is contacted with a zeolite comprising catalyst, for example a catalyst comprising ZSM-5, such as a catalyst comprising 50wt% of ZSM-5 and 50wt% ZSM-23, based on the zeolite content in the catalyst. Further olefinic product 65 is retrieved from reactor zone 60. Further olefinic product 65 comprises further ethylene and/or propylene. Optionally, further olefinic product 65 is recycled back (dotted line) to second separation unit 45. In that case, preferably part of further olefinic product 65 is withdrawn from the process as a purge stream to prevent the build-up of paraffinic hydrocarbons in further olefinic product 65.

In Figure 2, a process similar to that of Figure 1 is represented, however in the process of Figure 2, C4 hydrocarbon stream 255 is retrieved from second separation section 45, separate from any C5+ hydrocarbons, which may be retrieved via stream 257. C4 hydrocarbon stream 255 may be recycled back to etherification unit 5, where any iso-olefins in C4 hydrocarbon stream 255 are reacted to tert-alkyl ethers and the remainder, i.e. butene and mixed butanes may be withdrawn from process as part of iso-olefin-depleted olefinic product 30 and may be used as raffinate 2.

Examples

The invention is illustrated by the following non-limiting examples.

Example 1

Several molecular sieves were tested to show their ability to convert MTBE to an olefinic product. To test the molecular sieves for catalytic performance, a powder of the

respective molecular sieves was pressed into tablets and the tablets were broken into pieces and sieved. MTBE was reacted over the catalysts which were tested to determine their selectivity towards olefins, mainly ethylene and propylene from oxygenates. For the catalytic testing, the sieve fraction of 40-80 mesh was used. Prior to reaction, the molecular sieves were treated ex-situ in air at 550°C for 2 hours.

The reaction was performed using a quartz reactor tube of 1.8 mm internal diameter. The molecular sieve samples were heated in nitrogen to the reaction temperature and a mixture consisting of 6 vol% MTBE balanced in N₂ was passed over the catalyst at atmospheric pressure (1 bar). The Gas Hourly Space Velocity (GHSV) is determined by the total gas flow over the zeolite weight per unit time (ml.gzeolite⁻¹.h⁻¹). The gas hourly space velocity used in the experiments was 10000 (ml.gzeolite⁻¹.h⁻¹). The effluent from the reactor was analyzed by gas chromatography (GC) to determine the product composition. The composition has been calculated on a weight basis of all hydrocarbons analyzed. The composition has been defined by the division of the mass of specific product by the sum of the masses of all products. The effluent from the reactor obtained at several reactor temperatures was analyzed. The results are shown in Table 1.

Table 1

T	Catalyst	C2=	C3=	C4=	C5	Light ends	C6+	C4 paraffin
[°C]		[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]
420	SAPO-34	7.90	15.15	65.43	9.18	0.19	1.06	1.09
525	SAPO-34	9.41	18.17	50.01	14.78	1.57	2.58	3.49
420	ZSM-5*	10.86	28.10	15.93	8.13	0.12	23.56	13.31
525	ZSM-5*	26.77	38.11	11.46	2.69	0.03	13.01	7.92
525	ZSM-5 [#]	17.89	39.85	25.49	3.22	1.79	9.69	2.07
525	ZSM-23	20.73	42.89	29.00	2.05	0.59	3.62	1.12
525	ZSM-22	17.19	39.88	35.52	2.12	0.44	3.99	0.86

*SAR 80

[#]SAR 280

5 For all tested catalyst, the conversion of MTBE was complete. No MTBE or methanol was detected in the effluent of the reactor.

10 The zeolite catalysts, i.e. ZSM-5, ZSM-22 and ZSM-23, show a good conversion of the MTBE, including the isobutene part of the MTBE, to ethylene and propylene. An advantage of the one-dimensional zeolites having 10-membered ring channels, i.e. ZSM-22 and ZSM-23, is the lower paraffin make and C6+ make compared to the multi-dimensional ZSM5 zeolites.

15 By reducing the SAR of the ZSM-5 catalyst, the ethylene and propylene yield is improved, while significantly less C4 olefins are produced.

20 The non-zeolite SAPO-34 catalyst shows a low paraffin make and C6+ make, however is less suitable for converting iso-C4 olefins as can be seen from the relative high C4

olefin content in the effluent of the reactor. These C4 olefins are preferably subsequently converted in an OCP reactor over a zeolite catalyst. It will be clear from table 1, that zeolite catalyst show a better conversion of C4 olefins to the desired ethylene and propylene products. Increasing the reaction temperature, results in a reduction of the C4 olefin content in the effluent of the reaction.

Example 2

Several molecular sieves were tested to show their ability to convert a mixture of MTBE and methanol to an olefinic product. To test the molecular sieves for catalytic performance, a powder of the respective molecular sieves was pressed into tablets and the tablets were broken into pieces and sieved. A mixture of MTBE and methanol was reacted over the catalysts which were tested to determine their selectivity towards olefins, mainly ethylene and propylene from oxygenates. For the catalytic testing, the sieve fraction of 40-80 mesh was used. Prior to reaction, the molecular sieves were treated ex-situ in air at 550°C for 2 hours.

The reaction was performed using a quartz reactor tube of 1.8 mm internal diameter. The molecular sieve samples were heated in nitrogen to 525°C and a mixture consisting of 3 vol% MTBE and 3 vol% methanol, balanced in N₂ was passed over the catalyst at atmospheric pressure (1 bar). The Gas Hourly Space Velocity (GHSV) is determined by the total gas flow over the zeolite weight per unit time (ml.gzeolite⁻¹.h⁻¹). The gas hourly space velocity used in the experiments was 10000 (ml.gzeolite⁻¹.h⁻¹). The effluent from the reactor was analyzed by gas chromatography (GC) to determine the product composition. The composition has been

calculated on a weight basis of all hydrocarbons analyzed. The composition has been defined by the division of the mass of a specific product by the sum of the masses of all products. The results are shown in Table 2.

5 Table 2

T	Catalyst	C2=	C3=	C4=	C5	Light ends	C6+	C4 paraffin
[°C]		[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]
525	SAPO-34	18.11	22.08	44.94	8.23	2.94	1.64	2.05
525	ZSM-5*	25.72	37.64	11.57	3.24	0.65	13.79	7.41
525	ZSM-5 [#]	17.66	42.42	20.31	3.31	1.82	12.88	1.61
525	ZSM-23	21.45	46.66	21.09	2.77	0.81	6.16	1.06
525	ZSM-22	17.84	48.46	24.30	2.61	0.83	5.24	0.71

*SAR 80

[#]SAR 280

10 The zeolite catalysts do not show a significant change
in the obtained C2 to C4 olefinic product slate, when
methanol is added to the MTBE feed. As a result, it can be
expected that for an existing methanol based OTO process
using a zeolite catalyst, MTBE can be blended into the
methanol feed without requiring significant changes to the
15 process operation. In case of the SAPO-34 catalyst, the
ratio of propylene to ethylene obtained when using only
MTBE as a feed is higher than the ratio obtained from a
feed comprising a mixture of MTBE and methanol. As a result
it can be concluded that blending MTBE into a methanol
20 feedstock to a SAPO-34 based OTO process will result in an
improved ratio of propylene to ethylene without requiring
significant changes to the process operation.

C L A I M S

1. A process for preparing ethylene and/or propylene and an iso-olefin-depleted C4 olefinic product, comprising the steps of:

5 a) providing a C4 hydrocarbon stream, comprising normal olefins and iso-olefins;

b) subjecting the C4 hydrocarbon stream to an etherification process with methanol and/or ethanol wherein at least part of the iso-olefins are converted with methanol and/or ethanol to a tert-alkyl ether, and
10 retrieving an etherification product stream;

c) separating at least part of the etherification product stream into at least an ether-enriched stream and a first iso-olefin-depleted C4 olefinic product;

d) converting at least part of the tert-alkyl ether in the ether-enriched stream to ethylene and/or propylene by
15 contacting least part of the ether-enriched stream with a molecular sieve-comprising catalyst at a temperature in the range of from 350 to 1000 °C and retrieving a second olefinic product comprising ethylene and/or propylene.

20 2. A process according to claim 1, wherein the second olefinic product further comprises C4 olefins and wherein the process comprises the further step of:

e) contacting at least part of the C4 olefins in the second olefinic product with a zeolite-comprising catalyst
25 at a temperature in the range of from 350 to 1000 °C and converting at least part of the olefinic product into a further olefinic product comprising ethylene and/or propylene.

3. A process according to claim 2, wherein the zeolite-comprising 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.

5 4. A process according to claim 2 or 3, wherein the molecular sieve-comprising catalyst comprises at least one SAPO, AlPO, or MeAlPO type molecular sieve, preferably SAPO-34.

10 5. A process according to claim 2 or 3, wherein the molecular sieve-comprising catalyst in step (d) is a zeolite-comprising catalyst and the least part of the C4 olefins in the second olefinic product are contacted with the zeolite-comprising catalyst by providing at least part of the C4 olefins in the second olefinic product to step
15 (b).

6. A process according to any one of the preceding claims, wherein in step (d) comprises contacting an oxygenate-comprising feedstock with the molecular sieve-catalyst and wherein the oxygenate-comprising feedstock comprises tert-alkyl ether obtained in step (b) and one or more other
20 oxygenates, preferably at least one of methanol and dimethylether, more preferably methanol.

7. A process according to any one of the preceding claims, wherein the iso-olefins are converted with methanol and/or ethanol to the tert-alkyl ether by contacting the iso-olefin with methanol and/or ethanol in the presence of an etherification catalyst at a temperature in the range of
25 from 30 to 100°C, more preferably 40 to 80°C.

8. A process according to claim 10, wherein the
30 etherification catalyst is a protonated cation-exchange resin catalyst, preferably amberlyst-15.

9. A process according to any one of the preceding claims, wherein in step (b) the iso-olefins are converted with methanol to MTBE.

10. A process according to any one of the preceding claims, wherein the olefinic product comprises ethylene and at least part of the ethylene is further converted into at least one of polyethylene, mono-ethylene-glycol, ethylbenzene and styrene monomer.

11. A process according to any one of the preceding claims, wherein the olefinic product comprises propylene and at least part of the propylene is further converted into at least one of polypropylene and propylene oxide.

12. A process according to any one of the preceding claims, wherein at least part of the first iso-olefin-depleted C4 olefinic product is used as raffinate-2.

13. A process according to any one of the preceding claims, wherein at least part of the first iso-olefin-depleted C4 olefinic product is further converted into at least one of secondary butyl alcohol (SBA) and methyl ethyl ketone (MEK) or used as co-monomer in the production of polyethylene.

14. A process according to any one of the preceding claims, wherein the C4 hydrocarbon stream comprises C4 paraffins.

15. A process according to any one of the preceding claims, wherein the C4 hydrocarbon stream is a raffinate-1 stream.