

THIOETHERIFICATION OF MERCAPTANES IN C₄ HYDROCARBON MIXTURES

The invention relates to a process for the thioetherification of mercaptans with multiply unsaturated hydrocarbons, carried out in a reactor with addition of hydrogen using a heterogeneous catalyst and in the presence of 1-butene. Such a process is known from US5851383.

C₄-Hydrocarbons are compounds which consist exclusively of carbon and hydrogen and in which the number of carbon atoms per molecule is four. Important representatives of C₄-hydrocarbons are the alkenes and alkanes having four carbon atoms.

Mixtures of C₄-hydrocarbons are raw materials of downstream petrochemistry. They originate either from steam crackers (known as "cracking C₄") or from fluid catalytic crackers (known as "FCC C₄"). Mixtures of C₄ mixtures of various origins are also traded, known as "C₄ fraction". For the purposes of utilizing the individual components, the C₄ mixtures have to be separated into their constituents, preferably the pure constituents.

Mercaptans are compounds of the class R-SH, where R is an alkyl radical and S is sulphur and H is hydrogen. Mercaptans are also referred to as thiols. Important representatives of mercaptans are methyl mercaptan and ethyl mercaptan, also referred to as methanethiol and ethanethiol, respectively. Mercaptans occur in amounts of up to 1000 ppm as undesirable accompanying materials in C₄-hydrocarbon mixtures.

Industrial C₄-hydrocarbon mixtures from catalytic crackers (FCC C₄) or steam crackers (cracking C₄) usually contain not only saturated and monounsaturated compounds but also multiply unsaturated compounds. Before individual compounds can be isolated from these mixtures, it is frequently necessary to remove other compounds as completely as possible. This can be carried out by physical methods, e.g. distillation,

extractive distillation or extraction, or else by selective chemical reaction of the components to be removed. Particular attention has to be paid to the very complete removal of the impurities such as oxygen-, nitrogen- and sulphur-containing components present in the C₄-hydrocarbon mixture since these can act as catalyst
5 poisons and have adverse effects on the individual process steps. While these impurities are typically present only in traces in cracking C₄, they can be present in higher concentrations in FCC C₄ streams.

C₄-Hydrocarbon mixtures from steam crackers or fluid catalytic crackers typically have
10 the main components shown in Table 1. (Impurities not shown)

Components	Cracking C4	FCC C4
	[% by mass]	[% by mass]
Isobutane	1 – 3	20 - 40
n-Butane	6 - 11	5 – 15
1-Butene	14 – 20	10 - 20
2-Butenes	4 – 8	20 - 35
Isobutene	20 – 28	10 – 20
1,3- Butadiene	40 – 45	less than 1

Table 1: Typical compositions of cracking C₄ and FCC C₄

15 The composition of the raw materials can fluctuate greatly depending on the origin of the material. The C₄ components indicated are associated with hydrocarbons having fewer or more carbon atoms and also impurities such as mercaptans, sulphides, disulphides, nitrogen- and oxygen-containing compounds in small amounts.

20 The work-up of FCC C₄ can, in one variant, be carried out by firstly reducing the concentration of isobutane by means of a distillation step in a distillation to a value of

less than 5% by mass, particularly preferably less than 3% by mass. At the same time, the low boilers (e.g. C₃-hydrocarbons, light oxygen-, nitrogen- and sulphur-containing compounds) present in the mixture are removed or minimized. In the subsequent step, all high boilers (e.g. C₅-hydrocarbons, heavy oxygen-, nitrogen- and sulphur-containing
5 compounds) are removed at the bottom of a column. In the next step, isobutene is removed, e.g. by reacting it with methanol to form methyl tert-butyl ether (MTBE) and removing the latter by distillation. If pure isobutene is to be obtained, the methyl tert-butyl ether can subsequently be cleaved again to form isobutene and methanol.

- 10 To work the C₄ mixture up further, the remaining multiply unsaturated compounds have to be converted by means of a selective hydrogenation process into the corresponding monounsaturated and saturated compounds. 1-Butene and remaining isobutane can now be separated off in sufficient purity by distillation and the remaining 2-butenes and n-butane can be worked up further. The 2-butenes are frequently converted by
15 dimerization into octenes which are subsequently converted by means of hydroformylation into PVC plasticizer alcohols. The saturated C₄-hydrocarbons can, for example, be used as blowing agents.

If the concentration of the multiply unsaturated compounds is not reduced to a value
20 below 10 ppm in the selective hydrogenation process before the 1-butene is separated off, the purity requirements for 1-butene used in polymerizations are not attained. Furthermore, multiply unsaturated compounds suppress the catalytic activity of the catalysts for the dimerization of 2-butenes.

- 25 The work-up of C₄ streams from steam crackers or catalytic crackers is described in principle in K.-D. Wiese, F. Nierlich, *DGMK-Tagungsbericht* 2004-3, ISBN 3-936418-23-3.

The demands made of the selectivities in processes for the selective hydrogenation of
30 multiply unsaturated hydrocarbons are particularly great since products of value are

destroyed in the case of dehydration, i.e. hydrogenation of monounsaturated compounds, and isomerization of terminal double bonds to internal double bonds. At the same time, in the case of the fine purification of streams which already have a low content of multiply unsaturated compounds, the concentrations of multiply unsaturated compounds have to be reduced further to values below 10 ppmw.

Processes and catalysts for the selective hydrogenation of 1,3-butadiene in high concentration (from about 30 to 50%) in C₄ streams are described in EP0523482, DE3119850, EP0992284 and EP0780155.

In the case of catalytic C₄ streams, it is possible for not only the light sulphur-containing components which have been separated off by distillation in the low boiler removal, e.g. H₂S, COS or MeSH, and the relatively high-boiling sulphur compounds which have been separated off in the C₅ column, e.g. dimethyl disulphide, but also mercaptan-type intermediate boilers (e.g. ethanethiol) to be present. These cannot readily be removed by distillation from the C₄ stream. The presence of mercaptans is undesirable or interferes in the work-up of C₄ streams for a number of reasons:

- a) If mercaptans (e.g. ethanethiol) are present in the feed to the selective hydrogenation, these inhibit the catalytic reaction of 1,3-butadiene. Thus, the branched multiply unsaturated compounds can be present in the subsequent product (e.g. 1-butene) and place its purity at risk.
- b) If the multiply unsaturated compounds get into the feed for the oligomerization of the n-butenes because of incomplete reaction in the selective hydrogenation due to the mercaptan content, they deactivate the oligomerization catalyst.
- c) If the mercaptans get into the feed to the oligomerization of the n-butenes, they deactivate the oligomerization catalyst.

d) It is known that hydroisomerization-active catalysts can be formed by treatment of the selective hydrogenation catalyst with sulphur-containing components. Such a hydroisomerization catalyst which leads to undesirable isomerization of 1-butene to 2-butenes can be formed by the mercaptans present in the feed to the selective hydrogenation.

It is an object of the invention described here to circumvent these problems in the work-up of C₄ streams.

As prior art, in the presence of mercaptans it is possible to carry out a process involving extraction of the mercaptans by means of aqueous caustic alkali solution and subsequent oxidative conversion of the mercaptans into disulphides in order to lower the concentration of the mercaptans to values of about 5 – 15 ppm. Such a process is offered for industrial use by UOP LLC under the name MEROX®. (G. A. Dziabis, "UOP MEROX PROCESS" in Robert Meyers, Handbook of Petroleum Refining Processes, 3rd Edition, 2004 McGraw-Hill).

The disadvantage of the MEROX® process is that it not only requires a high outlay in terms of apparatus but also produces large amounts of water and caustic alkali streams which are costly to dispose of. In addition, complete removal of higher mercaptans (e.g. ethanethiol) is not ensured. It is therefore absolutely necessary to carry out additional measures for removing these residual amounts of mercaptans for further chemical use. This is achieved, for example, by adsorptive removal. Adsorptive processes for the desulphurization of C₄ streams are described in DE3914817C2 and DE19845857A1.

As an alternative, processes for the thioetherification of mercaptans with unsaturated hydrocarbons combined with hydrogenation of the multiply unsaturated hydrocarbons and at the same time isomerization of 1-butene to 2-butenes which reduce the concentration of the mercaptans to values below 1 ppm and that of the multiply unsaturated C₄-hydrocarbons to values below 10 ppm and also bring the concentration

of 1-butene into equilibrium with 2-butene are known.

US5851383 describes such a process for the simultaneous thioetherification of mercaptans to form relatively high-boiling thioethers, selective hydrogenation of multiply
5 unsaturated olefins in FCC C₃-C₅ streams and isomerization of light monoolefins. The process is carried out in the purely liquid phase in a fixed-bed reactor and nickel on aluminium oxide serves as catalyst. Hydrogen is added in a two-fold molar excess over diolefin.

10 US5463134 describes a process for the simultaneous acid-catalysed thioetherification of mercaptans with butenes to form relatively high-boiling thioethers and removal of olefins by oligomerization in the absence of hydrogen in a paraffin-rich C₄ stream. The process is carried out in the purely liquid phase in a fixed-bed reactor and an acidic ion exchanger serves as catalyst.

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WO 2003062178 describes a process for the pretreatment of C₄ streams for an alkylation of isobutane by means of butenes. Here, inter alia, a simultaneous thioetherification of mercaptans to form relatively high-boiling thioethers, a selective hydrogenation of multiply unsaturated olefins and isomerization of light monoolefins are
20 carried out. The process is carried out in the purely liquid phase in a fixed-bed reactor and nickel on aluminium oxide serves as catalyst. Hydrogen is added in a ten-fold molar excess over diolefin.

The disadvantage of the thioetherification processes mentioned is that isomerization of
25 1-olefins, especially 1-butene, takes place in addition to the reaction of the mercaptans and diolefins. This leads to a great decrease in the 1-olefin content, so that subsequent, targeted isolation of the 1-olefins is no longer possible. However, 1-olefins are products of value for which there is demand and can be isolated and utilized to bring a profit.

30 In WO2003062178 and in US5851383, hydrogenation of the monoolefins also takes

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place in parallel to the undesirable isomerization as a result of the hydrogen used in a molar excess. This leads to a significant reduction in the total monoolefin content in the product stream, and this is thus no longer available for downstream reactions (e.g. oligomerization).

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In the light of this prior art, it is an object of the invention to develop a process of the type mentioned at the outset in such a way that the value derived from the C₄ raw material stream used is increased.

- 10 This object is achieved by hydrogen being introduced into the reaction in such an amount that the molar ratio of hydrogen to multiply unsaturated hydrocarbons is not more than one.

The invention accordingly provides a process for the thioetherification of mercaptans
15 with multiply unsaturated hydrocarbons, carried out in a reactor with addition of hydrogen using a heterogeneous catalyst and in the presence of 1-butene, in which the molar ratio of hydrogen to multiply unsaturated hydrocarbons is not more than one.

The process of the invention is able to convert mercaptans into high-boiling thioethers
20 with complete conversion, at the same time virtually completely suppress any significant isomerization of 1-butene to internal butenes and also completely prevent hydrogenation of the butenes.

Contrary to the expectations of a person skilled in the art, it is shown in the context of
25 the present invention that mercaptans can be converted in the presence of 1,3-butadiene and hydrogen to below the detection limit into relatively high-boiling thioethers, with the isomerization of 1-butene being greatly suppressed and the hydrogenation of butenes being completely prevented. The detection limit of the mercaptans is at present about 50 ppbw, i.e. a proportion by weight of $50 \cdot 10^{-9}$.

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For the purposes of the present invention, the amount of hydrogen to be adhered to is at the most equimolar relative to the multiply unsaturated hydrocarbons present in the hydrocarbon mixture. The molar ratio of hydrogen to the multiply unsaturated hydrocarbons is preferably in the range from 0.01 to 0.8. It is particularly preferably in the range from 0.1 to 0.5.

A great advantage of this process is that, owing to the low proportion of hydrogen, 1-butene present in the C₄ stream is barely isomerized and continues to be available as product of value. In addition, the process makes it possible to dispense with a costly MEROX® scrub. Only the limits to the amount of hydrogen introduced which are to be adhered to precisely make it possible to etherify mercaptans in a process down to concentration values below 50 ppbw by means multiply unsaturated C₄-hydrocarbons to form high-boiling thioethers without hydrogenation of the monounsaturated butenes which are likewise present in the feed and appreciable isomerization of 1-butene occurring.

An important characteristic of the process is that no conversion of mercaptans occurs without hydrogen.

The multiply unsaturated hydrocarbons which are thioetherified with the mercaptans are preferably 1,3-butadiene and/or but-3-en-1-yne and/or 1,2-butadiene. These dienes and acetylenes are present in only small amounts, particularly in FCC-C₄, and in any case have to be hydrogenated completely downstream and are therefore no longer available as product of value. In the case of cracking C₄ streams which have a high 1,3-butadiene content, the 1,3-butadiene is removed separately beforehand and utilized. The residual butadienes remaining in the C₄ stream can then be used for the thioethertification.

A particular advantage of the process is that it is reactive not only in respect of the highly reactive mercaptan methanethiol but also in respect of higher mercaptans (e.g. ethanethiol). Thus, the mercaptans methanethiol and/or ethanethiol present in the

stream are preferentially thioetherified with multiply unsaturated hydrocarbons.

Carbon monoxide can optionally be additionally added to the hydrocarbon mixture to be hydrogenated. The content of carbon monoxide in the feed is in this case in the range
5 from 0.05 to 20 ppm of carbon monoxide, based on the mass of the hydrocarbon mixture. Preference is given to adding from 0.5 to 5 ppm of carbon monoxide. Added amounts above 20 ppm no longer improve the results. The carbon monoxide is introduced separately into the reactor or added to the inflowing C₄ stream.

- 10 Carbon monoxide acts as additional moderator which reduces isomerization of 1-butene to 2-butenes.

Suitable catalysts for the thioetherification are heterogeneous catalysts which contain a metal of group VIII of the Periodic Table of the Elements.

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In principle, the thioetherification of the invention is not tied to any particular group VIII metal catalyst. The metal is preferably present in supported form on an inert support material. The support material is, for example, aluminium oxide, silica gel or activated carbon. Preference is given to using aluminium oxide as support material.

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If the catalyst used is a catalyst based on palladium, it has a palladium concentration in the range from 0.01 to 3%, based on the mass of the support. The concentration is preferably in the range from 0.1 to 1%, very particularly preferably in the range from 0.3 to 0.5%. The catalyst has an internal surface area (determined by gas adsorption in
25 accordance with DIN ISO 9277) of from 50 to 400 m²/g, preferably from 100 to 300 m²/g, particularly preferably from 200 to 300 m²/g.

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Coated catalysts which comprise aluminium oxide as support and palladium as catalytically active metal have been found to be particularly advantageous for the thioetherification.

The entry temperature of the reactor feed is preferably in the range from 0 to 180°C, more preferably in the range from 60 to 150°C, particularly preferably in the range from 80 to 130°C. The pressure is preferably in the range from 0.2 to 5 MPa, more preferably
5 in the range from 0.6 to 4 MPa, particularly preferably in the range from 1 to 3 MPa. In all cases, the pressure has to be selected so that the hydrogen remains completely dissolved and no gas phase occurs in the reactor.

The thioetherification is preferably operated as a liquid-phase process. This means that
10 all components are present in the liquid phase over the catalyst or are introduced in liquid form into the reactor. In particular, it means that the hydrogen and optionally also the carbon monoxide are completely dissolved in the liquid phase.

The addition of hydrogen to the mixture of hydrocarbons to be hydrogenated is thus
15 effected in finely divided form and in such amounts that a homogeneous liquid phase is always present before entry into the hydrogenation reactor.

The hydrocarbon mixtures to be etherified can contain up to 1000 wppm of mercaptans, i.e. a proportion by weight of 10^{-3} . The thioetherification can be carried out in one or
20 more reaction stages. If the amount of mercaptans present in the feed is so great that the amount of hydrogen required is no longer soluble in the feed, the feed can be diluted by means of a recycle mode of operation. As an alternative, the hydrogen can be added in a plurality of partial amounts distributed over the length of the reactor or over the individual reaction stages.

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After complete conversion of the mercaptans into high-boiling thioethers, these thioethers can be separated off by distillation. This reduces the thioether content of the remaining C₄-hydrocarbon mixture to below 50 ppbw. Together with a possible low boiler removal upstream of the thioetherification reactor and a high boiler distillation
30 downstream of the thioetherification reactor, complete removal of all sulphur-containing

components from the C₄-hydrocarbon mixture is thus possible.

The concentration of multiply unsaturated olefins can be measured on-line by means of gas chromatography and the amount of hydrogen can be set exactly according thereto.

5 This likewise applies to the sulphur compounds.

The process is preferably applied to mercaptan-containing mixtures of C₄-hydrocarbons which originate from catalytic crackers (FCC C₄) or from steam crackers (cracking C₄). Of course, C₄ fraction can also be processed.

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The C₄-hydrocarbon mixture used as feed is preferably subjected beforehand to a removal of low boilers, in particular isobutane, by distillation.

As an alternative, the process is employed before the removal of isobutane.

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After the thioetherification according to the invention, at least one of the following process steps is carried out during the course of the further work-up and utilization of the C₄ stream:

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- removal of thioethers by distillation;
- removal of sulphur components by adsorption;
- selective hydrogenation of 1,3-butadiene to 1-butene and/or 2-butene;
- removal of 1-butene by distillation;
- oligomerization of 2-butenes to form olefins having more than 4 carbon

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- atoms;
- removal of n-butane and/or of isobutane by distillation;
- etherification of isobutene with methanol to form methyl tert-butyl ether (MTBE) and removal of the MTBE formed.

30 It is also possible to arrange a number of the processing steps indicated after the

thioetherification. The order can be chosen differently depending on the composition of the stream being processed.

In the processing of FCC C4, the following order is particularly preferred:

- 5 1. removal of thioethers by distillation;
2. removal of sulphur components by adsorption;
3. etherification of isobutene with methanol to form MTBE and removal of the
 MTBE formed;
- 10 4. selective hydrogenation of 1,3-butadiene to 1-butene and/or 2-butene;
5. removal of 1-butene by distillation;
6. oligomerization of 2-butenes to form olefins having more than 4 carbon
 atoms.
- 15 The removal of thioethers by distillation is customarily effected in a distillation column.
At the same time, the high boilers accompanying the C₄ stream, e.g. C₅-hydrocarbons,
are preferably removed together with the thioethers. The desulphurized C₄ stream is
taken off at the top of the distillation column.
- 20 A distillation column which is preferably used in this process step preferably has from
40 to 150 theoretical plates, preferably from 40 to 100 and particularly preferably from
50 to 80 theoretical plates. The reflux ratio is, depending on the number of theoretical
plates realised, the composition of the feed to the column and the required purities of
distillate and bottom product, preferably in the range from 0.5 to 5, particularly
25 preferably from 1 to 2.5. The reflux ratio is defined here as mass flow of the runback
divided by the mass flow of the distillate. The column is preferably operated at an
operation pressure of from 0.1 to 2.0 MPa (absolute), preferably from 0.5 to 1.2 MPa
(absolute). Heating of the column can be effected using, for example, steam. The
condensation can, depending on the operating pressure selected, be effected against
30 cooling brine, cooling water or air. However, the vapour from the top of the column can

also be heat-integrated with other columns in the process, e.g. with the column for separating off the isobutane. In this case, the condenser of the column serves simultaneously as vaporizer of the low boiler column. The bottom product can be utilized thermally or be used as starting material for other processes, for example in a synthesis gas plant.

In principle, all mercaptans which are harmful to the catalyst can be removed by means of the thioetherification according to the invention and the subsequent removal of the thioethers formed by distillation. However, since the effects of very small residual amounts of sulphur compounds can cause serious damage in the subsequent process, the removal of sulphur should be designed so as to be redundant. For this purpose, preference is given to providing an adsorber bed through which the overhead stream from the thioether removal by distillation is passed and very small residual amounts of sulphur-containing compounds are adsorbed in the process. In general, the adsorber adsorbs barely any material. In the case of an operational malfunction in the thioetherification or the subsequent distillation, the adsorber also keeps a large burden of sulphur compounds away from downstream catalytic processing steps. Suitable adsorbents for the desulphurization of C₄ streams are described in DE3914817C2 or in DE3825169A1 and DE19845857A1.

The adsorptive desulphurization is preferably carried out at a pressure of from 0.1 to 5 MPa and a temperature of from 20 to 160°C in the liquid phase. Typical trace components which are removed by the purification using the adsorber are, for example, sulphur compounds, nitrogen compounds, oxygen compounds and/or halogen compounds.

In the process of the invention, the isobutene present in the C₄ mixture obtained in this way is preferably reacted with methanol over acidic ion exchangers to give an MTBE reaction mixture and the MTBE is separated off from the C₄ mixture. In principle, all known processes for the synthesis of MTBE can be used for this purpose; for example,

the MTBE synthesis can be carried out in a manner analogous to the description in DE10102082A1.

Remaining butadiene which has not been reacted with the mercaptans to form
5 thioethers is preferably converted selectively into butenes in a hydrogenation step.
Since 1,3-butadiene is the most abundant butadiene in C₄ streams, it is hydrogenated
to 1-butene and/or 2-butene, if possible without hydrogenation of the remaining olefins.
The selective hydrogenation of the 1,3-butadiene is particularly preferably carried out at
about 40°C in the liquid phase, at a molar ratio of 1,3-butadiene to hydrogen of 1.1 and
10 with addition of 1 ppm of carbon monoxide over a palladium catalyst. Since these
reaction conditions differ significantly from those of the thioetherification, the two steps
cannot be carried out in the same reactor. A suitable process for the selective
hydrogenation of 1,3-butadiene to 1-butene and/or 2-butenes is disclosed in
DE102010030990A1. DE3143647A1 also discloses a suitable process.

15 The hydrogenation is carried out in the liquid phase over a palladium-containing fixed-
bed catalyst using hydrogen with addition of carbon monoxide as moderator. Hydrogen
and carbon monoxide are completely dissolved in the hydrocarbon mixture. The
amount of hydrogen added is at least the amount which is stoichiometrically required for
20 the hydrogenation of the multiply unsaturated compounds to the monoenes. It can be
calculated from the composition of the C₄ stream to be hydrogenated.

The amount of CO based on the mass of the C₄ stream to be hydrogenated is at least
0.05 ppm. Amounts of above 20 ppm normally do not lead to any further significant
25 improvement in the hydrogenation results, and amounts of from 0.05 to 10 ppm are
therefore preferred. The amount of CO which is optimally introduced in the respective
process can easily be determined experimentally, as described in DE3143647A1.

The catalyst for the selective hydrogenation comprises from 0.1 to 2% by mass of
30 palladium on a support. Such supports include, for example, aluminium oxide, silica gel,

aluminosilicate and activated carbon. The throughput of hydrocarbon per litre of catalyst used is preferably in the range from 5 to 300 litres.

The temperature at which the hydrogenation is carried out is from 0 to 75°C. Very particular preference is given to temperatures of about 40°C.

The process pressure has to be sufficiently high to maintain the liquid phase at the temperature selected and to bring a sufficient amount of hydrogen and carbon monoxide into solution. The reaction pressure is below 20 MPa, preferably below 6 MPa, more preferably below 2 MPa. A typical reaction pressure is 1.5 MPa.

The hydrogenation is preferably carried out in a plurality of stages, particularly preferably two stages. Hydrogen is fed in upstream of each of the reactors, and carbon monoxide is preferably fed into the first of the reactors. The reactors can be operated with recirculation of product.

After the selective hydrogenation, it is possible to separate off the product of value 1-butene. This can be carried out by distillation in one or more distillation columns. In a preferred embodiment, the 1-butene is separated in two distillation columns. In the first distillation column, a fraction rich in isobutane and 1-butene is firstly separated off as overhead product from the C4 mixture, and the stream rich in isobutane and 1-butene is then fractionated in a further distillation column. In this column, very pure 1-butene is obtained as bottom product. An isobutane-rich fraction which may additionally contain low boilers (for example C₃-hydrocarbons) is obtained as overhead product.

Pure 1-butene prepared in this work-up step preferably contains less than 5000 ppm by mass, more preferably less than 2000 ppm by mass and particularly preferably less than 1500 ppm by mass, of isobutene and is in demand as an intermediate. It can, for example, be used as comonomer in the preparation of polyethylene (LLDPE or HDPE) and also of ethylene-propylene copolymers. It is also used as alkylating agent and is a starting material for the preparation of 2-butanol, butene oxide, valeraldehyde.

Apart from the 1-butene, isobutane-rich fractions are also obtained in the work-up of the stream by distillation, depending on the starting composition of the C₄ hydrocarbons.

These isobutane-rich fractions can be purified further, preferably to give pure isobutane.

- 5 The isobutane obtained in the work-up preferably has a purity of at least 90% by mass of isobutane, particularly preferably 95% by mass of isobutane, and preferably contains less than 1000 wppm, particularly preferably less than 200 wppm, of olefins. Purification to give pure isobutane can, for example, be effected by complete hydrogenation of the alkenes still present to alkanes and subsequent distillation.

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Further information on carrying out the 1-butene removal may be found in DE102005062700A1 and DE102005062699A1.

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Oligomerizations are particularly susceptible to the catalyst poisons removed in the process of the invention. It is therefore advantageous to subject the C₄ stream which has been freed of mercaptans according to the invention to a subsequent oligomerization in the course of which 2-butenes and optionally also remaining 1-butene are oligomerized to form olefins having more than 4 carbon atoms.

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In this process step, the butenes are oligomerized over a heterogeneous catalyst comprising nickel, silicon and aluminium to give oligomers. The process underlying this process step is referred to in the literature as OCTOL® process which is described in Hydrocarbon Process., Int. Ed. (1986) 65 (2. Sect.1), pages 31 to 33, and also in the documents DE3914817, EP1029839 and DE102004018753.

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The oligomerization is carried out in the presence of heterogeneous nickel-containing supported catalysts. As support materials, the catalysts can comprise, for example, silicon dioxide and aluminium oxide, aluminosilicates or zeolites. Such catalysts are known in the technical literature and are described, for example, in DE4339713A1 or

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WO0137989.

The oligomerization is carried out at (reaction) temperatures of from 0 to 200°C, preferably from 50 to 130°C, and pressures of from 0.1 to 70 MPa, preferably from 0.1 to 10 MPa and particularly preferably from 0.5 to 3 MPa.

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Oligomers obtained by the oligomerization of the butenes are, in particular, olefins having eight, twelve, sixteen, twenty or more carbon atoms. These olefins can be used, for example, for preparing plasticizer alcohols (C₉- or C₁₃-alcohols) or alcohols (C₁₃-, C₁₇- or C₂₁-alcohols) for preparing raw materials for laundry detergents. Before further
10 processing, they are preferably worked up by distillation to give one or more fractions, and preferably separated into a fraction comprising dibutenes (mainly C₈-olefins), a fraction comprising tributene (C₁₂-olefins) and a fraction comprising higher oligomers (C₁₆₊-olefins). Isononyl alcohols which are used in large amounts as plasticizer alcohols can be obtained from the dibutenes by hydroformylation, hydrogenation and distillation.

15 Isotridecyl alcohols can be obtained from the tributenes by means of analogous reactions. Mixtures of high-purity paraffins can be obtained from the C₁₆₊-fraction by hydrogenation to the paraffins.

In a particularly preferred embodiment of the invention, a combined removal of
20 thioethers and 1-butene by distillation is carried out directly or indirectly after the thioetherification. In particular, this combined thioether and 1-butene removal takes place after a selective hydrogenation of butadiene. The combined removal of thioethers and 1-butene by distillation is preferably carried out in a side offtake column from the top of which 1-butene and optionally isobutane are taken off while the thioethers are
25 obtained at the bottom of the side offtake column. Raffinate III, viz. a C₄-hydrocarbon mixture which has been largely freed of butadiene, isobutene and 1-butene is taken off from the side offtake and, for example, passed to an oligomerization. The advantage of a combined removal of thioethers and 1-butene in a side offtake column is that a side offtake column incurs lower capital costs than two individual columns.

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If an MTBE synthesis is provided after the thioetherification, it is possible to separate off the methyl tert-butyl ether (MTBE) formed from isobutene and methanol together with the thioethers as an ether mixture by distillation. This preferred embodiment combines the isolation of MTBE by distillation and the removal of the thioethers in one step.

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However, the two ethers are not separated off separately in a side offtake column but instead in a conventional distillation column at the bottom of which an ether mixture consisting essentially of MTBE and thioethers is obtained. Since the thioethers are formed to a lesser extent than MTBE, the ether mixture can more accurately be described as an MTBE contaminated with thioethers.

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The expected contamination of the MTBE with thioethers is so low that the ether mixture can contribute to the fuel pool like a technical-grade MTBE. Separate separation of the ether mixture into thioethers and pure MTBE is therefore not necessary. For this reason, the separate removal of the thioethers is dispensed with because it can be carried out together with the MTBE isolation which is necessary in any case. The capital and operating costs of the plant are decreased thereby.

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Some preferred embodiments of the present invention will now be illustrated with the aid of the figures. The figures show:

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- Figure 1: Block diagram of a first embodiment;
- Figure 2: Block diagram of a second embodiment;
- Figure 3: Block diagram of a third embodiment;
- Figure 4: Block diagram of a fourth embodiment;
- Figure 5: Block diagram of a fifth embodiment.

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A block diagram of a first preferred embodiment by means of which the process of the invention can be carried out is shown in Figure 1. The mercaptan-containing C₄-hydrocarbon stream (10) is fed to the thioetherification step (S10). CO is optionally also

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fed to this step. Hydrogen (15) is also fed into the thioetherification step. In the thioetherification step, the mercaptans present are completely converted into thioethers, but 1,3-butadiene present is only partly converted.

5 The mercaptan-free stream (20) is fed to a distillation step (S20) in which the thioethers formed are separated off completely together with further relatively high-boiling components, e.g. C₅-hydrocarbons, as bottom stream (21). If no further high boilers are present, the thioethers can also be separated off later together with other high boilers formed in the sequence, e.g. MTBE. In the case of direct removal of high boilers (S20),
10 the now sulphur-free overhead stream (30) is fed to a hydrogenation step (S40). In this hydrogenation step, 1,3-butadiene still present is selectively hydrogenated by means of hydrogen (45) to 1- and 2-butene. CO is optionally also fed to this step. The now sulphur- and 1,3-butadiene-free C₄-hydrocarbon stream (40) can now be used as raw material in further chemical production processes.

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A second preferred embodiment of the process is shown in Figure 2. In this process variant, low boilers (12), predominantly isobutane, are separated off from the C₄-hydrocarbon stream (10) in a first distillation step (S1). The further work-up of the largely low boiler-free stream (11) is carried out as described above for Figure 1.

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A third preferred embodiment of the process is shown in Figure 3. In this process variant, the stream (30) after the high boiler removal (S20) is fed to an etherification stage (S30). In this stage, an alcohol (31), preferably methanol, is fed in and the isobutene obtained is converted into an ether, preferably methyl tert-butyl ether
25 (MTBE). The ether is separated off as high boiler (32) and the isobutene-free stream (35) is fed to the hydrogenation step (S40) which has already been described above.

A fourth preferred embodiment of the process is shown in Figure 4. As in the embodiment shown in Figure 3, this process encompasses an MTBE synthesis (S30)
30 arranged downstream of the thioetherification (S10). However, the thioethers are not

discharged in a separate separation stage corresponding to the distillation step (S20) of the third embodiment but are instead discharged together with the MTBE as high-boiling ether mixture (32) from the etherification step (S30).

- 5 A fifth preferred embodiment of the process is shown in Figure 5. The mercaptan-containing C₄-hydrocarbon stream (10) is fed to the thioetherification step (S10). CO is optionally also introduced into this step. Hydrogen (15) is also introduced into the thioetherification step. In the thioetherification step, the mercaptans present are completely converted into thioethers but 1,3-butadiene present is only partly reacted.

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The mercaptan-free stream (20) is then fed to a hydrogenation step (S40). In this hydrogenation step, 1,3-butadiene still present is selectively hydrogenated by means of hydrogen (45) to 1- and 2-butene. CO is optionally also introduced into this step. The now mercaptan- and 1,3-butadiene-free C₄-hydrocarbon stream (40) is then fed into a
15 side offtake column (S50) in which a combined removal of 1-butene and isobutane (41) via the top is effected. Raffinate III (50) is taken off from the side offtake. The thioethers 21 are taken off from the bottom of the side offtake column (S50). A combined removal of thioethers and 1-butene by distillation thus occurs in the side offtake column (50).

- 20 The present invention is illustrated below with the aid of examples. Alternative embodiments of the present invention can be obtained in an analogous way.

The thioetherification is carried out in a fixed-bed reactor having a heating jacket through which a heat transfer oil (Marlotherm SH from Sasol Olefins & Surfactants GmbH) flows. As catalyst, use is made of 0.54 litre of a coated catalyst comprising
25 0.5% of palladium on γ -aluminium oxide in extrudate form. The catalyst is the NOBLYST® H1427-1 which can be obtained from Evonik Industries AG.

- The specific internal surface area of the catalyst is about 250 m²/g and the pore volume is about 0.8 cm³/g. The thickness of the palladium layer is about 0.05 mm. To produce
30 the thioetherified mixture of C₄-hydrocarbons, raffinate III, 1,3-butadiene and

ethanethiol are mixed. Starting mixture and product mixture are analysed by gas chromatography.

Example 1 (according to the invention)

Component	1,3-Butadiene	1-Butene	2-Butenes	n-Butane	Ethanethiol
Feed [% by weight]	0.513	27.710	44.987	26.292	0.00210
Output [% by weight]	0.345	27.552	45.325	26.284	0.00000

5

Reaction conditions

T [°C]	P [bar]	Ratio of N(H ₂)/n(diene)	Isomerization of 1-Butene [%]
91	24	0.30	0.57

Example 2 (comparative example)

Component	1,3-Butadiene	1-Butene	2-Butenes	n-Butane	Ethanethiol
Feed [% by weight]	0.485	26.220	45.182	27.652	0.00200
Output [% by weight]	0.0	14.454	56.943	28.153	0.00010

Reaction conditions

T [°C]	P [bar]	Ratio of $n(\text{H}_2)/n(\text{diene})$	Isomerization of 1-Butene [%]
96	24	2.06	44.87

5

Example 3 (according to the invention)

Component	1,3-Butadiene	1-Butene	2-Butenes	n-Butane	Ethanethiol
Feed [% by weight]	0.502	29.489	46.949	22.502	0.00210
Output [% by weight]	0.325	29.276	47.381	22.461	0.00000

Reaction conditions

T [°C]	P [bar]	Ratio of $n(\text{H}_2)/n(\text{diene})$	Isomerization of 1-Butene [%]
122	24	0.30	0.75

Example 4 (according to the invention)

Component	1,3-Butadiene	1-Butene	2-Butenes	n-Butane	Ethanethiol
Feed [% by weight]	0.185	26.140	45.398	27.808	0.00200
Output [% by weight]	0.111	25.867	45.787	27.766	0.00000

Reaction conditions

T [°C]	P [bar]	Ratio of N(H ₂)/n(diene)	Isomerization of 1-Butene [%]
118	24	0.54	1.04

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Example 5 (according to the invention)

Component	1,3-Butadiene	1-Butene	2-Butenes	n-Butane	Methanethiol
Feed [% by weight]	0.509	31.570	43.547	23.874	0.00207
Output [% by weight]	0.386	31.349	43.899	23.868	0.00000

Reaction conditions

T [°C]	P [bar]	Ratio of n(H ₂)/n(diene)	Isomerization of 1-Butene [%]
105	24	0.29	0.70

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Example 6 (comparative example)

Component	1,3-Butadiene	1-Butene	2-Butenes	n-Butane	Ethanethiol
Feed [% by weight]	0.506	38.882	39.693	20.414	0.00200
Output [% by weight]	0.508	38.897	39.700	20.392	0.00199

Reaction conditions

T [°C]	P [bar]	Ratio of $n(\text{H}_2)/n(\text{diene})$	Isomerization of 1-Butene [%]
88	20	0.00	-0.04

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The tables of examples in each case show the significant composition of the feed stream and of the output stream of the fixed-bed reactor under various reaction conditions (without impurities).

- 10 In Example 1, the results of the thioetherification of about 5000 ppm of 1,3-butadiene and about 21 ppm of ethanethiol at an amount of hydrogen according to the invention are shown. It can be seen that ethanethiol can be etherified to a proportion by mass of 0 ppm without large amounts of the product of value 1-butene being lost. 1-Butene is reacted to an extent of only 0.59% (conversion = $(m_{\text{in}} - m_{\text{out}})/m_{\text{in}}$).

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- In Example 2, an excess of hydrogen over 1,3-butadiene of 2 (mol/mol) analogous to US5851383 is set. Here too, about 5000 ppm of 1,3-butadiene and about 20 ppm of ethanethiol are present in the feed. However, at this large amount of hydrogen, the proportion by mass of ethanethiol is reduced only to a value of about 1.0 ppm, which is not acceptable in the fine purification of C₄ fractions. In addition, the 1-butene content drops by more than 44%, while the n-butane content increases by 5000 ppm as a sign of total hydrogenation.
- 20

In Example 3, the temperature is increased to 122°C. Here too, at about 5000 ppm of 1,3-butadiene, about 21 ppm of ethanethiol can be thioetherified to a proportion by mass of 0 ppm without large proportions of the products of value being lost. 1-Butene is converted into 2-butenes to an extent of only 0.75%, while the proportion of butanes as a sign of total hydrogenation does not increase.

In Example 4, the feed concentration of 1,3-butadiene is reduced to about 1000 ppm and at the same time the ratio of hydrogen to diene is increased from 0.30 to 0.54. Here too, about 20 ppm of ethanethiol can be etherified to a proportion by mass of 0 ppm without large proportions of the products of value being lost. Due to the increased hydrogen/diene ratio, 1.04% of 1-butene are now reacted, but this is still a very low value. However, total hydrogenation to butanes does not take place.

Example 5 shows the results of the thioetherification of about 5000 ppm of 1,3-butadiene and about 21 ppm of methanethiol at an amount of hydrogen according to the invention. It can be seen that methanethiol, too, can be etherified to a proportion by mass of 0 ppm without large amounts of the product of value 1-butene being lost. 1-Butene is reacted to an extent of only 0.70%.

In Example 6, the reaction is carried out without hydrogen in the C₄-hydrocarbon stream. Here too, about 5000 ppm of 1,3-butadiene and about 20 ppm of ethanethiol are present in the feed. Without hydrogen, the proportion by mass of ethanethiol is not influenced, i.e. thioetherification does not take place without introduction of hydrogen.

Finally, the basic concept of the invention and their important uses will be summarized once more:

C₄-hydrocarbon streams contaminated with mercaptans, which usually originate from catalytic crackers, are unsuitable for oligomerization since the mercaptans seriously

damage the oligomerization catalyst. Hitherto, such streams were freed of mercaptans in a costly MEROX® process, but the removal of the mercaptans was incomplete. This required removal of the remaining mercaptans by adsorption before the oligomerization. The fundamental concept underlying the invention is to etherify all mercaptans present
5 in the C₄ stream to a higher molecular weight in order to make it possible to separate off the resulting thioethers by distillation. It has surprisingly been found that the thioetherification can be carried out over a heterogeneous catalyst when a very small amount of hydrogen is present. A great advantage of this process is that, owing to the low proportion of hydrogen, 1-butene present in the C₄ stream is barely isomerized and
10 is also available as product of value, and also total hydrogenation to butanes does not take place. In addition, the process makes a costly MEROX® scrub dispensable.

Claims

1. Process for the thioetherification of mercaptans with multiply unsaturated hydrocarbons, carried out in a reactor with addition of hydrogen using a heterogeneous catalyst and in the presence of 1-butene,
5 characterized in that the molar ratio of hydrogen to multiply unsaturated hydrocarbons is in the range from 0.01 to 0.8.
- 10 2. Process according to Claim 1, characterized in that the molar ratio of hydrogen to multiply unsaturated hydrocarbons is in the range from 0.1 to 0.5.
3. Process according to Claim 1 or 2, characterized in that the mercaptans are thioetherified with multiply unsaturated hydrocarbons which are selected from the
15 group consisting of: 1,3-butadiene, but-3-en-1-yne and 1,2-butadiene.
4. Process according to Claim 1, 2 or 3, characterized in that ethanethiol and/or methanethiol is/are thioetherified with multiply unsaturated hydrocarbons.
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5. Process according to any of the preceding claims, characterized in that it is carried out in the presence of carbon monoxide, with the content of carbon monoxide in the feed to the reactor being less than 20 ppm, based on the mass of the feed, whereby carbon monoxide is additionally added to the hydrocarbon mixture to be
25 hydrogenated.
6. Process according to any of the preceding claims, characterized in that the heterogeneous catalyst contains a metal of group VIII of the Periodic Table of
30 the Elements.

7. Process according to Claim 6,
characterized in that
the catalyst is a coated catalyst comprising aluminium oxide as support and
palladium as catalytically active metal.
- 5
8. Process according to any of the preceding claims,
characterized in that
the entry temperature of the feed into the reactor is in the range from 0°C to
180°C; preferably from 60°C to 150°C and very particularly preferably from 80°C
10 to 130°C.
9. Process according to any of the preceding claims,
characterized in that
it is operated as a liquid-phase process in such a way that the hydrogen is
15 completely dissolved in the liquid phase.
10. Process according to any of Claims 1 to 9,
characterized in that
a mixture of C₄-hydrocarbons is used as feed for the reactor.
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11. Process according to Claim 10,
characterized in that
the mixture used as feed is subjected beforehand to a removal of low boilers, in
particular isobutane, by distillation.
- 25
12. Process according to at least one of Claims 1 to 11,
characterized in that
the thioetherification is followed by at least one process step selected from the
group consisting of:
- 30
- removal of thioethers by distillation;

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- removal of sulphur components by adsorption;
- selective hydrogenation of 1,3-butadiene to 1-butene and/or 2-butene;
- removal of 1-butene by distillation;
- oligomerization of 2-butenes to form olefins having more than 4 carbon atoms;
- removal of n-butane and/or of isobutane by distillation;
- etherification of isobutene with methanol to form methyl tert-butyl ether (MTBE) and removal of the MTBE formed.