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,
characterized in that
the molar ratio of hydrogen to multiply unsaturated hydrocarbons is not more than one.

2. Process according to Claim 1, characterized in that the molar ratio of hydrogen to multiply unsaturated hydrocarbons is in the range from 0.01 to 0.8; preferably in that it 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 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.

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.

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 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.

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 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 completely dissolved in the liquid phase.

10. Process according to any of Claims 1 to 9,
characterized in that
a mixture of C_4-hydrocarbons is used as feed for the reactor.

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.

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:

- 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 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.

13. Process according to Claim 12, characterized in that a combined removal of thioethers and 1-butene by distillation follows the thioetherification.

14. Process according to Claim 12, where an etherification of isobutene by means of methanol to form methyl tert-butyl ether (MTBE) follows the thioetherification, characterized in that an ether mixture comprising MTBE and thioethers is subsequently separated off by distillation.

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, characterized in that the molar ratio of hydrogen to multiply unsaturated hydrocarbons is in the range from 0.01 to 0.8.

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 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.

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 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 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.

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 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 completely dissolved in the liquid phase.

10. Process according to any of Claims 1 to 9,
characterized in that
a mixture of C_4-hydrocarbons is used as feed for the reactor.

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.

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:

- 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 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.