Claims

1. A process for purifying hydrocarbon mixtures, in which a contaminated hydrocarbon mixture comprising hydrocarbons having three to eight carbon atoms is at least partly freed of contaminants by contacting it with a solid sorbent, the hydrocarbon mixture being exclusively in the liquid state during the contact with the sorbent,

   characterized in that

   the sorbent has the following composition that adds up to 100% by weight:

   - copper oxide: 10% to 60% by weight (calculated as CuO);
   - zinc oxide: 10% to 60% by weight (calculated as ZnO);
   - aluminium oxide: 10% to 30% by weight (calculated as Al_2O_3);
   - other substances: 0% to 5% by weight.

2. The process as claimed in claim 1,

   characterized in that

   the sorbent has the following composition that adds up to 100% by weight:

   - copper oxide: 30% to 45% by weight (calculated as CuO);
   - zinc oxide: 30% to 50% by weight (calculated as ZnO);
   - aluminium oxide: 10% to 15% by weight (calculated as Al_2O_3);
   - further metal oxides: 0% to 2% by weight;
   - graphite: 0% to 3% by weight;
   - other substances: 0% to 1% by weight.

3. The process as claimed in claim 1 or 2,

characterized in that

the contact is effected in the absence of hydrogen.

4. The process as claimed in claim 1, 2 or 3,

characterized in that

the contact is effected under the following conditions:

- temperature between 10°C and 150°C, especially between 20°C and 130°C and more preferably between 30°C and 120°C;
- pressure between 0.5 and 3.5 MPa;
- space-time yield (weight hourly space velocity - WHSV) between 0.5 h^{-1} and 7 h^{-1}.

5. The process as claimed in any of the preceding claims,

characterized in that

the contaminated hydrocarbon mixture contains at least one impurity from one of the following substance classes:

a) thiols having the general formula R-SH

where R may be an alkyl, aryl, cycloalkyl or alkenyl radical, where R is especially a methyl, ethyl, propyl, butyl, phenyl, cyclohexyl or butenyl radical;

b) disulphides having the general formula R-S-S-R'

where R and R' may be identical or different alkyl, aryl, cycloalkyl or alkenyl radicals, where R and R' are especially methyl, ethyl, propyl, butyl, phenyl, cyclohexyl or butenyl radicals;

c) sulphides having the general formula R-S-R'

where R and R' may be identical or different alkyl, aryl, cycloalkyl or alkenyl radicals, where R and R' are especially methyl, ethyl, propyl, butyl, phenyl, cyclohexyl or butenyl radicals;

d) substituted or unsubstituted sulphur-containing heterocycles, especially thiophenes and/or thiolanes.

6. The process as claimed in any of the preceding claims,

characterized in that

the proportion by weight of the contaminants in the contaminated hydrocarbon mixture, based on the total weight thereof, is less than 0.2% by weight, more preferably below 100 ppm by weight and most preferably below 10 ppm by weight.

7. The process as claimed in any of the preceding claims,

characterized in that

the contaminated hydrocarbon mixture is obtained from a pre-purification stage which pre-purifies a more highly contaminated raw material mixture to obtain the contaminated hydrocarbon mixture.

8. The process as claimed in claim 7,

characterized in that

the sorbent is used irreversibly.

9. The process as claimed in any of the preceding claims,

characterized in that

the contaminated hydrocarbon mixture fulfils one of the following specifications A, B, C and D, each of which adds up to 100% by weight, the stated proportions by weight each being based on the total weight of the contaminated hydrocarbon mixture:

Specification A:

- isobutane 20% to 40% by weight, preferably 30% to 37% by weight;
- n-butane 5% to 18% by weight, preferably 8% to 10% by weight;
- 1-butene 5% to 15% by weight, preferably 12% to 14% by weight;
- isobutene 12% to 25% by weight, preferably 15% to 20% by weight;
- 2-butenes 9% to 40% by weight, preferably 20% to 30% by weight;
- 1,3-butadiene 0% to 3% by weight, preferably 0.5% to 0.8% by weight;
- water 0% to 1% by weight, preferably less than 0.1% by weight;
- contaminants, especially sulphur-contained hydrocarbons, less than 0.5% by weight, preferably less than 0.2% by weight;

Specification B:

- isobutane 0.6% to 8% by weight, preferably 1% to 7% by weight;
- n-butane 0.5% to 8% by weight, preferably 4% to 7% by weight;
- 1-butene 9% to 25% by weight, preferably 10% to 20% by weight;
- isobutene 10% to 35% by weight, preferably 20% to 30% by weight;
- 2-butenes 3% to 15% by weight, preferably 5% to 10% by weight;
- 1,3-butadiene 25% to 70% by weight, preferably 40% to 50% by weight;
- water 0% to 1% by weight, preferably less than 0.5% by weight;
- contaminants, especially sulphur-contained hydrocarbons, less than 0.5% by weight, preferably less than 0.2% by weight;

Specification C:

- isobutane 0.6% to 8% by weight, preferably 1% to 7% by weight;
- n-butane 0.5% to 15% by weight, preferably 4% to 13% by weight;
- 1-butene 9% to 40% by weight, preferably 10% to 35% by weight;
- isobutene 10% to 55% by weight, preferably 20% to 50% by weight;
- 2-butenes 3% to 25% by weight, preferably 5% to 20% by weight;
- 1,3-butadiene 0% to 1% by weight, preferably less than 0.8% by weight;
- water 0% to 1% by weight, preferably less than 0.5% by weight;

- contaminants, especially sulphur-contained hydrocarbons, less than 0.5% by weight, preferably less than 0.2% by weight;

Specification D:

- n-butane 10% to 30% by weight, preferably 25% to 30% by weight;
- 1-butene 0.2% to 45% by weight, preferably 5% to 30% by weight;
- 2-butenes 35% to 85% by weight, preferably 50% to 75% by weight;
- water 0% to 1% by weight, preferably less than 0.1% by weight;
- contaminants, especially sulphur-containing hydrocarbons, less than 0.5% by weight, preferably less than 0.1% by weight.

10. The process as claimed in any of the preceding claims,

characterized in that

the hydrocarbon mixture which has been at least partly freed of contaminants is subjected to at least one of the workup steps enumerated below:

a) extraction of 1,3-butadiene present in the hydrocarbon mixture;

b) selective hydrogenation of diolefins and/or acetylenes present in the hydrocarbon mixture to olefins;

c) oligomerization of olefins present in the hydrocarbon mixture to corresponding oligomers;

d) distillative removal of 1-butene and/or isobutane present in the hydrocarbon mixture, especially with the purpose of obtaining 1-butene and/or isobutane in high purity;

e) removal of isobutene present in the hydrocarbon mixture by conversion of the isobutene with water to tert-butanol and/or with methanol to methyl tert-butyl ether;

f) dehydrogenation of butanes present in the hydrocarbon mixture to butenes;

g) oxidative dehydrogenation of butenes present in the hydrocarbon mixture to butadiene;

h) alkylation of n-butene present in the hydrocarbon mixture with isobutane likewise present;

i) oxidation of hydrocarbons having four carbon atoms present in the hydrocarbon mixture for preparation of maleic anhydride.

11. Use of a solid having the following composition:

- copper oxide: 10% to 60% by weight (calculated as CuO);
- zinc oxide: 10% to 60% by weight (calculated as ZnO);
- aluminium oxide: 10% to 30% by weight (calculated as Al_2O_3);
- other substances: 0% to 5% by weight

for purification of liquid hydrocarbon mixtures comprising hydrocarbons having three to eight carbon atoms.

Claims

1. A process for purifying hydrocarbon mixtures, in which a contaminated hydrocarbon mixture comprising hydrocarbons having three to eight carbon atoms is at least partly freed of contaminants by contacting it with a solid sorbent, the hydrocarbon mixture being exclusively in the liquid state during the contact with the sorbent,

   wherein

   the sorbent has the following composition that adds up to 100% by weight:

   - copper oxide: 10% to 60% by weight (calculated as CuO);
   - zinc oxide: 10% to 60% by weight (calculated as ZnO);
   - aluminium oxide: 10% to 30% by weight (calculated as Al_2O_3);
   - other substances: 0% to 5% by weight,

   wherein the contaminated hydrocarbon mixture contains at least one impurity from one of the following substance classes:

   a) thiols having the general formula R-SH

      where R may be an alkyl, aryl, cycloalkyl or alkenyl radical, where R is especially a methyl, ethyl, propyl, butyl, phenyl, cyclohexyl or butenyl radical;

   b) disulphides having the general formula R-S-S-R'

      where R and R' may be identical or different alkyl, aryl, cycloalkyl or alkenyl radicals, where R and R' are especially methyl, ethyl, propyl, butyl, phenyl, cyclohexyl or butenyl radicals;

   c) sulphides having the general formula R-S-R'

      where R and R' may be identical or different alkyl, aryl, cycloalkyl or alkenyl radicals, where R and R' are especially methyl, ethyl, propyl, butyl, phenyl, cyclohexyl or butenyl radicals;

   d) substituted or unsubstituted sulphur-containing heterocycles, especially thiophenes and/or thiolanes,

wherein the contact is effected under the following conditions:

- temperature between 30°C and 120°C;
- pressure between 0.5 and 3.5 MPa;
- space-time yield (weight hourly space velocity - WHSV) between 0.5 h^{-1} and 7 h^{-1},

and wherein the contaminated hydrocarbon mixture fulfils one of the following specifications A, B, C and D, each of which adds up to 100% by weight, the stated proportions by weight each being based on the total weight of the contaminated hydrocarbon mixture:

Specification A:

- isobutane 20% to 40% by weight, preferably 30% to 37% by weight;
- n-butane 5% to 18% by weight, preferably 8% to 10% by weight;
- 1-butene 5% to 15% by weight, preferably 12% to 14% by weight;
- isobutene 12% to 25% by weight, preferably 15% to 20% by weight;
- 2-butenes 9% to 40% by weight, preferably 20% to 30% by weight;
- 1,3-butadiene 0% to 3% by weight, preferably 0.5% to 0.8% by weight;
- water 0% to 1% by weight, preferably less than 0.1% by weight;
- contaminants, especially sulphur-contained hydrocarbons, less than 0.5% by weight, preferably less than 0.2% by weight;

Specification B:

- isobutane 0.6% to 8% by weight, preferably 1% to 7% by weight;
- n-butane 0.5% to 8% by weight, preferably 4% to 7% by weight;
- 1-butene 9% to 25% by weight, preferably 10% to 20% by weight;
- isobutene 10% to 35% by weight, preferably 20% to 30% by weight;
- 2-butenes 3% to 15% by weight, preferably 5% to 10% by weight;
- 1,3-butadiene 25% to 70% by weight, preferably 40% to 50% by weight;
- water 0% to 1% by weight, preferably less than 0.5% by weight;
- contaminants, especially sulphur-contained hydrocarbons, less than 0.5% by weight, preferably less than 0.2% by weight;

Specification C:

- isobutane 0.6% to 8% by weight, preferably 1% to 7% by weight;
- n-butane 0.5% to 15% by weight, preferably 4% to 13% by weight;
- 1-butene 9% to 40% by weight, preferably 10% to 35% by weight;
- isobutene 10% to 55% by weight, preferably 20% to 50% by weight;
- 2-butenes 3% to 25% by weight, preferably 5% to 20% by weight;
- 1,3-butadiene 0% to 1% by weight, preferably less than 0.8% by weight;
- water 0% to 1% by weight, preferably less than 0.5% by weight;
- contaminants, especially sulphur-contained hydrocarbons, less than 0.5% by weight, preferably less than 0.2% by weight;

Specification D:

- n-butane 10% to 30% by weight, preferably 25% to 30% by weight;
- 1-butene 0.2% to 45% by weight, preferably 5% to 30% by weight;
- 2-butenes 35% to 85% by weight, preferably 50% to 75% by weight;
- water 0% to 1% by weight, preferably less than 0.1% by weight;
- contaminants, especially sulphur-containing hydrocarbons, less than 0.5% by weight, preferably less than 0.1% by weight.

2. The process as claimed in claim 1,

wherein the sorbent has the following composition that adds up to 100% by weight:

- copper oxide: 30% to 45% by weight (calculated as CuO);
- zinc oxide: 30% to 50% by weight (calculated as ZnO);
- aluminium oxide: 10% to 15% by weight (calculated as Al_2O_3);
- further metal oxides: 0% to 2% by weight;
- graphite: 0% to 3% by weight;
- other substances: 0% to 1% by weight.

3. The process as claimed in claim 1 or 2,

wherein the contact is effected in the absence of hydrogen.

4. The process as claimed in any of the preceding claims,

wherein the proportion by weight of the contaminants in the contaminated hydrocarbon mixture, based on the total weight thereof, is less than 0.2% by weight, more preferably below 100 ppm by weight and most preferably below 10 ppm by weight.

5. The process as claimed in any of the preceding claims,

wherein the contaminated hydrocarbon mixture is obtained from a pre-purification stage which pre-purifies a more highly contaminated raw material mixture to obtain the contaminated hydrocarbon mixture.

6. The process as claimed in claim 5,

wherein the sorbent is used irreversibly.

7. The process as claimed in any of the preceding claims,

wherein the hydrocarbon mixture which has been at least partly freed of contaminants is subjected to at least one of the workup steps enumerated below:

a) extraction of 1,3-butadiene present in the hydrocarbon mixture;

b) selective hydrogenation of diolefins and/or acetylenes present in the hydrocarbon mixture to olefins;

c) oligomerization of olefins present in the hydrocarbon mixture to corresponding oligomers;

d) distillative removal of 1-butene and/or isobutane present in the hydrocarbon mixture, especially with the purpose of obtaining 1-butene and/or isobutane in high purity;

e) removal of isobutene present in the hydrocarbon mixture by conversion of the isobutene with water to tert-butanol and/or with methanol to methyl tert-butyl ether;

f) dehydrogenation of butanes present in the hydrocarbon mixture to butenes;

g) oxidative dehydrogenation of butenes present in the hydrocarbon mixture to butadiene;

h) alkylation of n-butene present in the hydrocarbon mixture with isobutane likewise present;

i) oxidation of hydrocarbons having four carbon atoms present in the hydrocarbon mixture for preparation of maleic anhydride.