Claims

1. Process for purifying hydrocarbon mixtures, in which a contaminated hydrocarbon mixture comprising olefins having three to eight carbon atoms is at least partly freed of sulphur-containing contaminants by contacting it with a solid sorbent, the hydrocarbon mixture being exclusively in the liquid state during the contact with the sorbent, and wherein the sorbent has the following composition that adds up to 100% by weight:

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

~~characterized in that~~ wherein

the contaminated hydrocarbon mixture is contacted with the solid sorbent in the presence of hydrogen, wherein the contaminated hydrocarbon mixture, immediately prior to contact with the solid sorbent, contains hydrogen in a concentration, based on the total mass of the contaminated hydrocarbon mixture, between 1 ppm by weight and 10 000 ppm by weight, and wherein the contact is effected under the following conditions:

- temperature between 10°C and 150°C;
- pressure between 0.5 and 3.5 MPa;
- space-time yield (weight hourly space velocity - WHSV) between 0.5 h^{-1} and 20 h^{-1}.

2. Process according to Claim 1,

~~characterized in that~~ wherein

~~the contaminated hydrocarbon mixture, immediately prior to contact with the solid sorbent, contains hydrogen in a concentration, based on the total mass of the contaminated hydrocarbon mixture, between 1 ppm by weight and 10 000 ppm by weight, preference being given to a~~ the concentration of hydrogen lies between 10 ppm by weight and 500 ppm by weight.

3. Process according to Claim 2,

~~characterized in that~~ wherein

the hydrogen is fully dissolved in the liquid contaminated hydrocarbon mixture.

4. Process according to Claim 2 or 3,

~~characterized in that~~ wherein

said concentration of hydrogen is established by adding hydrogen to the contaminated hydrocarbon mixture immediately prior to the contact, whereas the contaminated hydrocarbon mixture prior to addition of the hydrogen contains less than 1 ppm by weight of hydrogen.

5. Process according to Claim 1 or any of Claims 2 to 4,

~~characterized in that~~ wherein

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

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

6. Process according to Claim 1 or any of Claims 2 to 5,

~~characterized in that~~ wherein

~~the contact is effected under the following conditions:~~

- ~~the~~ temperature ~~between 10°C and 150°C, especially~~ lies 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 20 h^{-1}~~.

7. Process according to Claim 1 or any of Claims 2 to 6,

~~characterized in that~~ wherein

the contaminated hydrocarbon mixture contains, as sulphur-containing contaminant, at least one compound 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.

8. Process according to Claim 7,

~~characterized in that~~ wherein

the proportion by weight of the sulphur-containing contaminants, calculated as sulphur, 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.

9. Process according to Claim 8,

~~characterized in that~~ wherein

the contaminated hydrocarbon mixture is freed by the contact with the sorbent of at least 90% by weight of the sulphur-containing contaminants present in the contaminated hydrocarbon mixture, preferably of at least 95% by weight.

10. Process according to Claim 8 or 9,

~~characterized in that~~ 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.

11. Process according to Claim 10,

~~characterized in that~~ wherein

the sorbent is used irreversibly.

12. Process according to Claim 4 or any of Claims 5 to 11,

~~characterized in that~~ 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 15% to 45% by weight, preferably 25% to 35% by weight;
- n-butane 5% to 18% by weight, preferably 8% to 10% by weight;
- 1-butene 5% to 20% 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;

Specification D:

- isobutane 0% to 20% by weight, preferably 0% to 5% by weight;
- n-butane 10% to 35% by weight, preferably 25% to 30% by weight;
- 1-butene 0.2% to 45% by weight, preferably 3% 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;
- sulphur-containing impurities less than 0.5% by weight, preferably less than 0.1% by weight;
- hydrogen less than 1 ppm by weight.

13. Process according to Claim 12,

~~characterized in that~~ wherein

the contact with the sorbent results in conversion of less than 5% of the 1-butene present in the contaminated hydrocarbon mixture.

14. Process according to at least one of Claims 1 to 11,

~~characterized in that~~ wherein

the contaminated hydrocarbon mixture comprises 1-butene and in that by contact with the sorbent less than 5 % of 1-butene comprised in the contaminated hydrocarbon mixture is converted.

15. *Process according to Claim 1 or any of Claims 2 to 14,*

~~characterized in that~~ 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;