METHOD FOR THE SELECTIVE HYDROGENATION OF POLYUNSATURATED HYDROCARBONS IN OLEFIN-CONTAINING HYDROCARBON MIXTURES

The present invention describes a process for the parallel selective hydrogenation of branched and unbranched multiply unsaturated C_4-C_6-hydrocarbons in olefin-containing hydrocarbon mixtures with minimization of hydrogenation and isomerization of the olefins present in the stream.

Industrial C_4-C_6-hydrocarbon mixtures from catalytic crackers or steam crackers 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 effected by physical methods such as distillation, extractive distillation or extraction and also by means of a selective chemical reaction of the components to be removed.

C_4 streams from steam crackers or catalytic crackers can, for example, have the following composition:

Component	Proportion by mass/%
1,3-Butadiene	42
Isobutene	25
1-Butene	16
cis-2-Butene	4
trans-2-Butene	5
n-Butane	5
Isobutane	2
Acetylenes	0.9
C5+	0.1

branched multiply unsaturated C_5-hydrocarbons to be removed together to concentrations of < 10 ppm in one process without a significant loss of monounsaturated hydrocarbons occurring or significant isomerization of α-olefins to internal olefins taking place because of the different reaction rates and the different adsorption constants of these groups of hydrocarbons (cf. Alves et al., *Chem. Eng. J.* **2004**, *99*, 45).

It was therefore an object of the invention to develop a process for the selective hydrogenation of unbranched multiply unsaturated C_4-hydrocarbons in low concentration in C_4-hydrocarbon mixtures, which likewise hydrogenates branched multiply unsaturated C_5-hydrocarbons present in the feed stream without the abovementioned undesirable secondary reactions occurring.

Contrary to the expectations of a person skilled in the art, it has been shown according to the present invention that unbranched multiply unsaturated C_4-hydrocarbons and branched multiply unsaturated C_5-hydrocarbons which occur as constituents in a C_4-hydrocarbon stream can be hydrogenated to concentration values of < 10 ppm in one process. Here, the undesirable hydrogenation of the monounsaturated butenes which are likewise present in the feed stream and the isomerization of 1-butene occur to only a very minor extent.

In one aspect, ~~The present invention accordingly provides~~there is provided a process for the selective hydrogenation of unbranched, multiply unsaturated C_4-hydrocarbons and branched, multiply unsaturated C_5-hydrocarbons in hydrocarbon mixtures with addition of hydrogen and carbon monoxide and using heterogeneous hydrogenation catalysts in a hydrogenation reactor, wherein the ratio of the volume of the feed stream into the hydrogenation reactor to