

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

5 The present invention describes a process for the
parallel selective hydrogenation of branched and
unbranched multiply unsaturated C₄-C₆-hydrocarbons in
olefin-containing hydrocarbon mixtures with
minimization of hydrogenation and isomerization of the
10 olefins present in the stream.

Industrial C₄-C₆-hydrocarbon mixtures from catalytic
crackers or steam crackers usually contain not only
saturated and monounsaturated compounds but also
15 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
20 distillation or extraction and also by means of a
selective chemical reaction of the components to be
removed.

C₄ streams from steam crackers or catalytic crackers
25 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

The work-up of this mixture can, in one variant, be carried out by firstly reducing the concentration of 1,3-butadiene by means of extractive distillation or by means of a selective hydrogenation process for high butadiene concentrations to a value of about 1%. At the same time, the acetylenes present in the mixture are removed or converted into monounsaturated/saturated compounds. The C₄ mixture is referred to as raffinate 1 by those skilled in the art. In the next step, isobutene is removed, e.g. by converting it by means of methanol into methyl tert-butyl ether (MTBE) and removing the latter by distillation. If pure isobutene is to be isolated, the methyl tert-butyl ether can subsequently be cleaved to form isobutene and methanol again.

For the further work-up of the C₄ mixture, now raffinate 2, the multiply unsaturated compounds still remaining have to be converted by means of a selective hydrogenation process into the corresponding monounsaturated and saturated compounds. Now, 1-butene and isobutene can be separated off in sufficient purity by distillation and the remaining 2-butenes and the n-butane can be worked up further. The 2-butenes are frequently converted by 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 compound is not reduced to a value of less than 10 ppm before the 1-butene is separated off in the selective hydrogenation process, the purity requirements for 1-butene used in polymerizations are not met. Furthermore, multiply unsaturated compounds reduce the catalytic activity of these catalysts for the dimerization of the 2-butenes.

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 selectivities in the processes for selective
5 hydrogenation of multiply unsaturated hydrocarbons have
to meet particularly demanding requirements since
products of value are destroyed in the event of
overhydrogenation, i.e. the hydrogenation of
monounsaturated compounds, and also isomerization of
10 terminal double bonds to internal double bonds. At the
same time, the concentrations of multiply unsaturated
compounds have to be reduced to values of usually < 1%
in the case of streams having high contents of multiply
unsaturated compounds and to < 10 ppm in the fine
15 purification of streams which already have a low
content of multiply unsaturated compounds.

Processes and catalysts for the selective hydrogenation
of 1,3-butadiene in high concentration (~30-50%) in C₄
20 streams are described in EP 0 523 482, DE 31 19 850,
EP 0 992 284 and EP 780 155.

C₄ streams can contain branched multiply unsaturated
compounds having more than 4 carbon atoms, e.g.
25 isoprene, in addition to unbranched multiply
unsaturated compounds such as 1,3-butadiene. The
presence of branched multiply unsaturated compounds is
undesirable in the work-up of C₄ streams or interferes
in this work-up for a number of reasons:

30 a) If branched multiply unsaturated compounds
(e.g. isoprene) are present in the feed to the MTBE
synthesis, these react with methanol to form the
corresponding methyl ethers (e.g. 3-methoxy-3-
methylbut-1-ene). If the MTBE is subsequently cleaved
35 again, the branched multiply unsaturated compounds can
reappear in the product and endanger its purity.

b) If the branched multiply unsaturated compounds
get into the feed to the oligomerization of the

n-butenes, they deactivate the oligomerization catalyst.

The selective hydrogenation of both the unbranched and
5 branched multiply unsaturated compounds could overcome
these problems in the work-up of C₄ streams. Thus, in
the presence of unbranched and branched multiply
unsaturated hydrocarbons, a process for the selective
hydrogenation of unbranched multiply unsaturated C₄-
10 hydrocarbons and a selective hydrogenation process for
the hydrogenation of branched multiply unsaturated C₅-
hydrocarbons would follow one another in order to
reduce the concentration of both the branched and
unbranched multiply unsaturated C₄- and C₅-hydrocarbons
15 to values of < 10 ppm.

EP 0 081 041 describes a process for the selective
hydrogenation of multiply unsaturated or acetylenic
compounds in low concentrations (< 21%, preferably
20 < 1%) in C₄ streams. The process is carried out in a
purely liquid phase and palladium on an inert support,
e.g. aluminium oxide, serves as catalyst. To suppress
the unwanted hydrogenation of monounsaturated
compounds, carbon monoxide is added in an amount of
25 from 0.05 to 20 ppm.

A process for the selective hydrogenation of branched
multiply unsaturated C₅-hydrocarbons in C₅-hydrocarbon
mixtures is described in EP 0 556 025.

30 In Alves et al., *Chem. Eng. J.* 2004, 99, 45, it is
stated that 1,3-butadiene can be hydrogenated in a C₄
stream in the presence of isoprene to concentration
values of < 10 ppm, but the isoprene concentration is
35 not reduced to similarly low values.

A person skilled in the art would therefore not expect
unbranched multiply unsaturated C₄-hydrocarbons and

branched multiply unsaturated C₅-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
5 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).

10 It was therefore an object of the invention to develop a process for the selective hydrogenation of unbranched multiply unsaturated C₄-hydrocarbons in low concentration in C₄-hydrocarbon mixtures, which likewise hydrogenates branched multiply unsaturated C₅-
15 hydrocarbons present in the feed stream without the abovementioned undesirable secondary reactions occurring.

Contrary to the expectations of a person skilled in the
20 art, it has been shown according to the present invention that unbranched multiply unsaturated C₄-hydrocarbons and branched multiply unsaturated C₅-hydrocarbons which occur as constituents in a C₄-hydrocarbon stream can be hydrogenated to concentration values of
25 < 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.

30 In one aspect, there is provided a process for the selective hydrogenation of unbranched, multiply unsaturated C₄-hydrocarbons and branched, multiply unsaturated C₅-hydrocarbons in hydrocarbon mixtures with
35 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

the volume of the hydrogenation catalyst per hour of residence time is not more than 30 l/lh.

For the purposes of the present invention, unbranched, multiply unsaturated C₄-hydrocarbons are, in particular,
5 1,3-butadiene, but-3-en-1-yne and 1,2-butadiene.

For the purposes of the present invention, branched, multiply unsaturated C₅-hydrocarbons are, in particular, isoprene, 2-methylbut-1-en-3-yne, 2-methylbuta-
10 1,2-diene, pent-4-en-2-yne and 3-methylbut-3-en-1-yne.

The ratio of the volume of the feed stream into the hydrogenation reactor to the volume of the hydrogenation catalyst per hour of residence time
15 $[V_{\text{feed}}/(V_{\text{cat}} \cdot \text{RET})]$, where RET = residence time] is important to the process of the invention and the success of the selective hydrogenation. This parameter is known to those skilled in the art as LHSV (liquid hourly space velocity). The volumes mentioned are in
20 litres.

For the purposes of the present invention, the term "feed stream" refers to the totality of all liquid or gaseous reaction components which are fed into the hydrogenation reactor. These are, in particular, the
25 hydrocarbon mixtures in which, inter alia, the unbranched, multiply unsaturated C₄-hydrocarbons and branched, multiply unsaturated C₅-hydrocarbons are present but also hydrogen and carbon monoxide.

30 According to the present invention, the LHSV to be adhered to is not more than 30 l/lh, in particular from 10 l/lh to 25 l/lh.

Only when the precise limits to the LHSV are adhered to can unbranched multiply unsaturated C₄-hydrocarbons and
35 branched multiply unsaturated C₅-hydrocarbons which occur as constituents in a C₄-hydrocarbon stream be hydrogenated to concentration values of < 10 ppm in one process without appreciable hydrogenation of the

monounsaturated butenes which are likewise present in the feed stream and isomerization of 1-butene occurring. The proportion of unbranched multiply unsaturated C₄-hydrocarbons and branched multiply unsaturated C₅-hydrocarbons is, in particular, reduced to less than 10 ppm by the process of the invention.

The process of the invention is operated as a liquid-phase process, i.e. the reaction components are present in the liquid phase over the catalyst or are introduced in the liquid phase into the hydrogenation reactor.

The addition of hydrogen to the hydrocarbon mixture to be hydrogenated is thus effected in finely divided form and in such amounts that a homogeneous liquid phase is always present before entry into the hydrogenation reactor. The stoichiometric ratio (**molar ratio**) of hydrogen to the hydrocarbons to be hydrogenated is in the range from 2 to 1. The ratio is preferably in the range from 1.5 to 1. It is particularly preferably in the range from 1.2 to 1.

Carbon monoxide is additionally added to the hydrocarbon mixture to be hydrogenated. The content of carbon monoxide in the feed stream is in the range 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. Amounts above 20 ppm no longer improve the hydrogenation results.

Heterogeneous hydrogenation catalysts are used as catalysts in the process of the invention. In particular, the hydrogenation catalysts are catalysts based on palladium, but the process of the invention is not tied to any particular palladium catalyst. The palladium 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. The catalyst has a palladium

concentration which is in the range from 0.01 to 3%, based on the mass of the support. It 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 a BET
5 surface area (determined by gas adsorption in 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.

10 The temperature at which the feed stream enters the hydrogenation reactor is usually in the range from 0 to 100°C, preferably in the range from 20 to 80°C, particularly preferably in the range from 30 to 60°C. The pressure is usually in the range from 2 to 50 bar,
15 preferably in the range from 6 to 30 bar, particularly preferably in the range from 10 to 25 bar.

The hydrogenation can be carried out in one or more reaction stages. If the amount of multiply unsaturated
20 hydrocarbons present in the feed stream is so large that the necessary stoichiometric amount of hydrogen is no longer soluble in the feed stream, the feed stream can be diluted by means of the recycle mode. The hydrocarbon mixtures to be hydrogenated can contain up
25 to 20% of multiply unsaturated hydrocarbons.

Even without further explanations, it is assumed that a person skilled in the art can utilize the above description in its widest scope. The preferred
30 embodiments and examples are therefore merely to be interpreted as a descriptive disclosure which is not limiting in any way.

The present invention is illustrated below with the aid of examples.

35 Alternative embodiments of the present invention can be derived in an analogous way.

Examples:

The hydrogenation is carried out in a fixed-bed reactor provided with a heating jacket through which a heat transfer oil (Marlotherm SH from Sasol Olefins & Surfactants GmbH) flows. 0.54 litre of a coated catalyst containing 0.5% of palladium on γ -aluminium oxide in extrudate form is used as catalyst. 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 the hydrocarbon mixture to be hydrogenated, raffinate 1, 1,3-butadiene and isoprene are mixed. Starting mixture and product mixture are analysed by gas chromatography.

Example 1 (according to the invention)

Component	1,3-Butadiene	Iso-prene	1-Butene	Isobutene + balance	2-Butene	C5-mono-enes	n-butane
Feed [% by wt]	0.2083	0.2451	28.8933	47.9032	13.4133	0	9.3368
Output [% by wt]	0.0006	0.0009	28.3557	47.7165	14.0890	0.2310	9.6063

Reaction conditions

T [°C]	P [bar]	LHSV/l/(l*h)	Ratio of n(H ₂)/n(diene)	CO concentration [ppm]	Conversion of 1-butene
30	20	15	1.1	1.3	1.8%

Example 2 (comparative example)

Component	1,3-Butadiene	Iso-prene	1-Butene	Isobutene + balance	2-Butene	C5-mono-enes	n-butane
Feed [% by wt]	0.2403	0.2374	29.5211	47.7619	12.9960	0	9.2433

Output [% by wt]	0.0004	0.0220	29.3735	47.7233	13.1949	0.2171	9.4688
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Reaction conditions

T [°C]	P [bar]	LHSV/l/(l*h)	Ratio of n(H ₂) / n(diene)	CO con- centration [ppm]	Conversion of 1-butene
30	20	36	1.1	1.0	0.5%

5 **Example 3 (according to the invention)**

Component	1,3- Buta- diene	Iso- prene	1- Butene	Isobutene + balance	2- Butene	C5- mono- enes	n- butane
Feed [% by wt]	0.1936	0.2421	29.5211	43.2569	13.1741	0	13.6122
Output [% by wt]	0.0006	0.0010	29.2902	43.2533	13.5940	0.2408	13.6201

Reaction conditions

T [°C]	P [bar]	LHSV/l/(l*h)	Ratio of n(H ₂) / n(diene)	CO con- centration [ppm]	Conversion of 1-butene
40	20	16	1.1	1.3	0.78%

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Example 4 (according to the invention)

Component	1,3- Buta- diene	Iso- prene	1- Butene	Isobutene + balance	2- Butene	C5- mono- enes	n- butane
Feed [% by wt]	0.0956	0.2419	28.5082	43.9973	12.0909	0	15.0648
Output [% by wt]	0.0006	0.0010	27.9097	43.9966	12.7672	0.2557	15.0692

Reaction conditions

T [°C]	P [bar]	LHSV/l/(l*h)	Ratio of n(H ₂)/n(diene)	CO con- centration [ppm]	Conversion of 1-butene
40	20	16	1.5	1.3	2.1%

The tables in the examples in each case show the composition of the feed stream and of the output stream of the fixed-bed reactor under various reaction conditions. Example 1 shows the results of the hydrogenation of about 2000 ppm of 1,3-butadiene and about 2400 ppm of isoprene at an LHSV according to the invention. It can be seen that both 1,3-butadiene and isoprene can be hydrogenated to a proportion by mass of less than 10 ppm without large proportions of the products of value 1-butene and 2-butene being lost. 1-Butene is converted to an extent of only 1.8% (conversion = $(m_{in}-m_{out})/m_{in}$).

In Example 2, an LHSV of 36 l/(l*h) analogous to EP 0 081 041 is set. Here too, about 2000 ppm of 1,3-butadiene and about 2400 ppm of isoprene are present in the feed stream. However, at this high LHSV, the proportion by mass of isoprene is reduced only to a value of about 200 ppm, which is not acceptable in the fine purification of C₄ fractions.

In Example 3, the temperature is increased to 40°C. Here too, about 2000 ppm of 1,3-butadiene and about 2300 ppm of isoprene can be hydrogenated to a proportion by mass of less than 10 ppm without large proportions of the products of value being lost. 1-Butene is converted to an extent of 0.78%, while 2-butene again displays a negative conversion. The proportion of butanes as an indication of total hydrogenation likewise increases only by a value of less than 100 ppm.

In Example 4, the 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 1.1 to 1.5. Here too, about 2000 ppm of 1,3-butadiene and about 2300 ppm of isoprene can be hydrogenated to a proportion by mass of less than 10 ppm without large proportions of the products of value being lost. As a result of the increased hydrogen/diene ratio, 2.1% of 1-butene are now converted, but this is still a very low value. The conversion of 2-butene at the same time becomes more negative, which indicates increased isomerization of 1-butene to 2-butene. However, total hydrogenation to butanes takes place to only an insignificant extent.

Claims

1. Process for the selective hydrogenation of unbranched, multiply unsaturated C₄-hydrocarbons and branched, multiply unsaturated C₅-hydrocarbons in hydrocarbon mixtures with addition of hydrogen and carbon monoxide and using heterogeneous hydrogenation catalysts in a hydrogenation reactor, characterized in that the ratio of the volume of the feed stream into the hydrogenation reactor to the volume of the hydrogenation catalyst per hour of residence time is not more than 30 l/lh.
2. Process according to Claim 1, characterized in that the ratio of the volume of the feed stream into the hydrogenation reactor to the volume of the hydrogenation catalyst per hour of residence time is in the range from 10 to 25 l/(lh).
3. Process according to Claim 1 or 2, characterized in that the content of carbon monoxide in the feed stream is from 0.05 to 20 ppm, based on the mass of the hydrocarbon mixture.
4. Process according to one or more of Claims 1 to 3, characterized in that the heterogeneous hydrogenation catalyst is a palladium catalyst.
5. Process according to one or more of Claims 1 to 4, characterized in that the temperature at which the feed stream enters the hydrogenation reactor is from 0 to 100°C.
6. Process according to one or more of Claims 1 to 5, characterized in that it is operated as a liquid-phase process.