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(54) Title: PROCESS FOR REDUCING THE HALOGEN CONTENT OF A HYDROCARBON PRODUCT STREAM BY CONTACTING WITH A METAL

(57) Abstract: The present invention provides a process for reducing the halogen content of a hydrocarbon product stream which is obtained by a hydrocarbon conversion process in which use is made of a halogen-containing acidic ionic liquid catalyst, which process comprises the steps of: (a) contacting the hydrocarbon product stream with a metal selected from the group consisting of Group IA and IIA elements of the Periodic Table, and/or an alloy comprising at least one of these metals; and (b) recovering from step (a) a hydrocarbon-rich phase having a halogen content which is smaller than the halogen content of the hydrocarbon product stream.



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**PROCESS FOR REDUCING THE HALOGEN CONTENT OF A
HYDROCARBON PRODUCT STREAM BY CONTACTING WITH A METAL**

Field of the invention

The present invention provides a process for reducing the halogen content of a hydrocarbon product stream.

5 Background of the invention

In a variety of hydrocarbon conversion processes use is nowadays made of halogen-containing acidic ionic liquid catalysts. Although such catalysts can effectively be used to produce useful hydrocarbon products such as gasoline or gasoline components, a major disadvantage of the use of these catalysts is that the hydrocarbon products so produced may have undesirably high halogen contents. In this respect it is observed that the presence of organic chlorides in for instance a gasoline may generate during combustion corrosive and harmful materials such as hydrogen chloride and/or dioxins. It is therefore important that hydrocarbon products intended to be used as gasolines or gasoline components only contain a very small amount of halogens.

20 A process for reducing the concentration of organic halide in a product stream of an alkylation process wherein use is made of a halide-based acidic ionic liquid catalyst has been described in US 2009/0264694. In said process the concentration of organic halide is reduced by contacting at least part of the product stream with a hydrotreating catalyst in the presence of hydrogen and under hydrotreating conditions. Such a process has the drawback that hydrotreating processes are expensive

because the application of high pressures and the need for equipment to recycle excess of hydrogen.

Further, in US 2010/0147746 a process for reducing halide concentrations in a hydrocarbon product has been described, wherein at least a portion of the hydrocarbon is contacted with an aqueous caustic solution under conditions to reduce the halide concentration in the hydrocarbon product. A considerable disadvantage of such a caustic process is the fact that preferred conditions include temperatures of no less than 200°C or greater.

In another process, described in WO 2009/079107, the organic halide contamination is reduced by the use of molecular sieves, which absorb in their pores molecules of a certain size.

Further, in US 5,928,500, hydrocarbon feedstreams contaminated with organic halides, are treated with a metal selected from nickel, cobalt or iron, or mixtures thereof on a porous high surface area refractory support in order to remove the halide contaminant(s).

In US 4,755,628 a multi-step dehalogenation process is disclosed using sodium dispersions at elevated temperatures.

The prior art processes are generally batch processes, mostly not very suitable for continuous production environments, or the processes do not remove the organic halides completely or make use of expensive catalysts.

Clearly, there is a need in the art to provide an effective process for reducing the halogen content of hydrocarbon product streams that overcomes the above-mentioned disadvantages.

Summary of the invention

It has been found that the halogen content, in particular the chloride content, of a hydrocarbon product stream can attractively be reduced, in particular in a continuous process, when the hydrocarbon product stream is contacted with a particular metal and/or alloy supported on a carrier.

Accordingly, the present invention provides a process for reducing the halogen content of a hydrocarbon product stream which is obtained by a hydrocarbon conversion process in which use is made of a halogen-containing acidic ionic liquid catalyst, which process comprises the steps of:

(a) contacting the hydrocarbon product stream with a metal selected from the group consisting of Group IA and IIA elements of the Periodic Table, and/or an alloy comprising at least one of these metals; and

(b) recovering from step (a) a hydrocarbon-rich phase having a halogen content which is smaller than the halogen content of the hydrocarbon product stream.

The use of the selected metal and/or alloy supported on a carrier establishes under attractively mild conditions a highly effective reduction of the halogen content, in particular reduction of the content of organic chlorides, of a hydrocarbon product stream that is produced by means of a halogen-containing acidic ionic liquid catalyst.

Detailed description of the invention

In the process according to the invention, a hydrocarbon product stream is contacted in step (a) with a metal selected from the group consisting of Group IA and IIA elements of the Periodic Table, and/or an alloy comprising at least one of these metals. The metal or alloy to be selected can suitably applied in solid form

or in the form of a liquid (e.g. melted droplets).
According to an embodiment of the invention, the metal
and/or alloy to be selected is supported on a carrier.
The carrier can suitably be chosen from a wide variety of
5 carriers. Examples of suitable carrier materials include
but are not limited to aluminas, silicas, alumina-
silicas, zeolites, carbon composites, titanias,
zirconias, carbonates, and sulphides. Suitable examples
of carrier materials have also been described in the
10 following documents: B.M. Vanderbilt, Ing. Eng. Chem.
49(1957)696 and US 4,977,124, which are hereby
incorporated by reference.

In the present process use can be made of a metal
and/or an alloy. The metal is selected from the group
15 consisting of Group IA and IIA elements of the Periodic
Table. Preferably, the metal is selected from the
Group IA elements of the Periodic Table. Preferred Group
IA elements are sodium and potassium. In case, two or
more metals are present in the form of an alloy, the
20 alloy comprises at least one metal from Group IA or IIA
of the Periodic Table, preferably at least one metal from
Group IA. Examples of such alloys include Na-K, Na-Al,
Na-Hg, Na-Bi, Na-Sn and Na-Pb. Even more preferred alloys
comprise only Group IA or IIA elements of the Periodic
25 Table, more preferred only Group IA metal elements. A
preferred alloy is an alloy of sodium or potassium, i.e.
Na-K.

There are prior art processes using sodium or
sodium-potassium alloy (see e.g. US 1,934,068 and
30 Chemosphere, vol. 41, 2000, p. 819-824) for reducing the
concentration of halides in other types of hydrocarbon
feedstreams. In those processes unsupported metal / alloy
is used, resulting in product mixtures containing highly

reactive materials. According to an embodiment of the present invention the metal / alloy is supported on a carrier, which is much easier to handle in the product mixtures.

5 In the process according to the present invention preferably use is made in step (a) of a liquid metal or liquid alloy. Reference herein to a liquid metal or liquid alloy is to a metal or alloy that is at least liquid at the temperature at which the metal or alloy is contacted with the hydrocarbon product stream in step (a). Without wishing to be bound to any particular theory, it is believed that by using a liquid metal or alloy, any metal halides formed, which remain on the surface of the liquid metal or alloy may be transported into the bulk of the liquid metal or alloy, thereby reducing metal halide concentration at the metal or alloy surface.

15 Suitably, in step (a) the molar ratio of the metal and/or alloy to halogen present in the hydrocarbon product stream is at least 1, more preferably at least 2. Suitably, said molar ratio can be in the range of from 1-50000. Preferably, the molar ratio of the metal and/or alloy to halogen present in the hydrocarbon product stream is in the range of from 2-10000.

25 In step (b) a hydrocarbon-rich phase having a halogen content which is smaller than the halogen content of the hydrocarbon product stream is recovered.

30 In an embodiment of this invention, in a batchwise process, in step (b) also a metal-rich and/or alloy-rich phase is recovered from the mixture obtained in step (a). Preferably, in such a case, at least part of the metal-rich and/or alloy-rich phase is recycled to step (a) to maintain the amount of metal and/or alloy in step (a) at a sufficient level. Generally, such metal-rich

and/or alloy-rich phase will comprise hydrocarbons and one or more metals and one or more metal halides. As indicated before, the metal and/or alloy can be supported, in solid form or in liquid form. The metal or alloy may be present in the form of a mixture with corresponding metal halides. The temperature of the metal-rich and/or alloy-rich phase can be lowered to solidify the liquid metal and/or alloy. These phases can be separated using any suitable liquid/liquid separator or liquid/solid separator as known in the art e.g. cyclone or centrifugal separators.

According to an embodiment of this invention, the metal and/or alloy is supported in solid form or in liquid form (see e.g. GB14116317) to avoid the above described separation process and enable application in a continuous process. The supported metal/alloy is placed as a bed in an absorber. Preferably, the bed is either a fixed bed or a fluidized bed through which the hydrocarbon product stream is transported. Further preferred, to enable continuous operation without need to stop the chloride absorption, two beds or more are placed in series whereby the first bed can be replaced when saturated - e.g. most or all metal has been converted into metal salts and the bed lost most of its activity - and the second bed becomes the first bed and the refilled bed becomes the second bed. Typical drawings are shown in Figures 1 and 2 for upward and downward flow, respectively, whereby a fluidized bed option is only possible in an upward flow (Fig 1). See for example also: http://www.anikshree.com/carbon_molecular_sieve.php or US 5177298 for typical arrangements of two absorption beds whereby one is used for absorption and the other one for refilling with fresh absorbent.

Reference, herein to a hydrocarbon-rich phase is to a phase comprising more than 50 mol% of hydrocarbons, based on the total moles of hydrocarbon, metal and/or alloy. Reference, herein to a metal-rich and/or alloy-rich phase produced in batch mode is to a phase comprising more than 50 mol% of metal and/or alloy, based on the total moles of metal and/or alloy, metal halide(s) and hydrocarbon.

In step (a) a temperature can suitably be applied of up to 300°C. Preferably, in step (a) a temperature is applied of less than 200°C, more preferably of less than 150°C. Most preferably, the temperature in step (a) is in the range of from 20-100°C. It is a major advantage of the present invention that low temperatures, including temperatures as low as ambient temperature, can be applied to establish attractive reductions in halogen contents.

In a particular attractive embodiment of the present invention use is made of the alloy of sodium and potassium, also referred to a Na-K. This alloy is liquid over a large compositional range, in particular the alloy comprising in the range of from 40% to 90% potassium by weight is liquid at temperatures as low as -12°C. Preferably, step (a) of the process is performed using an alloy of sodium and potassium and a temperature is applied in step (a) in the range of from -12°C to 150°C, wherein the alloy of sodium and potassium is liquid at the applied temperature of step (a). In case a liquid metal or alloy is present on a carrier, it is present as a film or droplets.

Suitably, the contacting in step (a) is established by mixing the hydrocarbon product stream and the metal and/or alloy. Efficient mixing can be established by

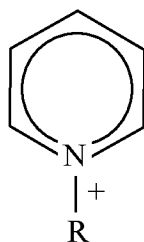
using appropriate mixing means. In case the metal and/or alloy is unsupported, examples of such suitable mixing means include, for instance, dynamic and static mixers and stirred reactors. In case the metal and/or alloy is supported, mixing is preferably achieved by using a bed of the metal/and or alloy on a support, whereby the flow rate of the hydrocarbon product stream is such that efficient mass transfer is achieved according to design rules to be used as known by persons skilled in the art, see e.g. Perry's Chemical Engineers' Handbook, 7th ed (1997).

It is desired to achieve in step (a) a high surface area of the metal and/or alloy and to remove the metal halide(s) that are formed in step (a). Suitably, this can be achieved by amongst others (1) efficient mixing; (2) using the metal and/or alloy in liquid form; (3) dispersing the metal and/or alloy droplets; and/or (4) supporting the metal and/or alloy on a support with high surface area.

Examples of hydrocarbon conversion processes from which the hydrocarbon product stream is obtained include alkylation of paraffins, alkylation of aromatics, (co)polymerisation, oligomerisation, dimerisation, isomerisation, acetylation, olefin hydrogenation, metatheses, and hydroformylation. Preferably, the hydrocarbon conversion process is an alkylation process. Preferably, alkylation processes of paraffins or aromatics. Hence, the hydrocarbon product stream to be treated in accordance with the present invention is preferably an alkylate-comprising stream obtained from an alkylation process, more preferably a high octane alkylate stream.

Ionic liquids are known in the art for their ability to catalyse alkylation reactions. A wide variety of halogen-containing acidic ionic liquid catalysts can be used in hydrocarbon conversion processes. The ionic

liquid catalyst can suitably be a composite ionic liquid comprising cations derived from a hydrohalide of an alkyl-containing amine, imidazolium or pyridine. Preferably, the cations comprise nitrogen atoms, which are saturated with four substituents, among which there is at least one hydrogen atom and one alkyl group. More preferably, the alkyl substituent is at least one selected from methyl, ethyl, propyl, butyl, amyl, and hexyl groups. Examples of suitable cations include triethyl-ammonium (NEt_3H^+) and methyl- diethyl-ammonium cations (MeNEt_2H^+) or



The anions of the composite ionic liquid are preferably aluminium based Lewis acids, in particular aluminium halides, preferably aluminium (III) chloride. Due the high acidity of the aluminium chloride Lewis acid it is preferred to combine the aluminium chloride, or other aluminium halide, with a second or more metal halide, sulphate or nitrate to form a coordinate anion, in particular a coordinate anion derived from two or more metal halides, wherein at least one metal halide is an aluminium halide. Suitable further metal halides, sulphates or nitrates, may be selected from halides, sulphates or nitrates of metals selected from the group

consisting of Group IB elements of the Periodic Table, Group IIB elements of the Periodic Table and transition elements of the Periodic Table. Examples or suitable metals include copper, iron, zinc, nickel, cobalt, molybdenum, or platinum. Preferably, the metal halides, sulphates or nitrates, are metal halides, more preferably chlorides or bromides, such as copper (I) chloride, copper (II) chloride, nickel (II) chloride, iron (II) chloride. Preferably, the molar ratio of the aluminium compound to the other metal compounds in the range of from 1:100-100:1, more preferably of from 1:1-100:1, or even more preferably of from 2:1-30:1.

In accordance with the present invention hydrocarbon product streams can be obtained having a halogen content of less than 20 ppm by weight.

Legend of figures:

Figure 1. Schematic representation of fixed and/or fluidized bed operation with upward flow of the hydrocarbon product stream.

Figure 2. Schematic representation of fixed bed operation with downward flow of the hydrocarbon product stream.

Example

The invention is illustrated by the following non-limiting batch example.

A 200 mL Schlenk-vessel was loaded with 4.68 g of 10 wt% Na-K alloy supported on alumina (by a method such as described in e.g. GB14116317), in the glovebox.

50 mL of alkylate obtained from an alkylation process (containing 103 mg Cl/kg) was added and the mixture was stirred gently with a magnetic stirring bar at room temperature. A white precipitate appeared and after 30 minutes stirring was stopped and the solids allowed settling down. A 6 mL sample was taken from the

clear solution for total chlorine analysis and stirring was continued. Using the same procedure a further sample was taken after 1 hrs. Coulometric Total Chloride analysis based on ASTM D6721, adapted for use on liquid and gaseous samples, was carried out of the various samples, and the results are shown in Table 1

Table 1

Alkylate (g) Total Chloride content (ppm) before treatment	103	103	103
Time (hr)	0	0.5	2
Total Chloride content (ppm) after treatment	103	1	0.7

It will be clear from the results shown in Table 1 that the process in accordance with the present invention brings a highly attractive reduction of chlorides at a temperature as low as room temperature. By placing the supported metal or alloy in an absorbent bed a continuous removal of organic chlorides can be achieved.

C L A I M S

1. A process for reducing the halogen content of a hydrocarbon product stream which is obtained by a hydrocarbon conversion process in which use is made of a halogen-containing acidic ionic liquid catalyst, which process comprises the steps of:

(a) contacting the hydrocarbon product stream with a metal selected from the group consisting of Group IA and IIA elements of the Periodic Table, and/or an alloy comprising at least one of these metals; and

(b) recovering from step (a) a hydrocarbon-rich phase having a halogen content which is smaller than the halogen content of the hydrocarbon product stream.

2. A process according to claim 1, wherein in step (b) also a metal-rich and/or alloy-rich phase is recovered from the mixture obtained in step (a).

3. A process according to claim 1 or 2, wherein at least part of the metal-rich and/or alloy-rich phase is recycled to step (a).

4. A process according to claim 1, wherein the metal or alloy in step (a) is supported on a carrier.

5. A process according to claim 4, wherein in step (a) the supported metal or alloy is placed in a fixed or fluidized bed through which the hydrocarbon product stream is transported.

6. A process according to claim 4 or 5, wherein the process is a continuous process.

7. A process according to any one of claims 1-6, wherein the metal is selected from the Group IA elements of the Periodic Table, and/or an alloy comprising at least one metal of the Group IA elements of the Periodic Table.

8. A process according to claim 7, wherein use is made of an alloy which comprises sodium and potassium.

9. A process according to any one of claims 1-8, wherein use is made in step (a) of a liquid metal or liquid alloy.

10. A process according to any one of claims 1-9, wherein in step (a) a temperature is applied of less than 200°C.

11. A process according to claim 10, wherein the temperature is in the range of from 20-100°C.

12. A process according to any one of claims 1-11, wherein the molar ratio of the metal and/or alloy to halogen present in the hydrocarbon product stream is at least 1.

13. A process according to any one of claims 1-12, wherein the molar ratio of the metal and/or alloy to halogen present in the hydrocarbon product stream is in the range of from 1-50000.

14. A process according to any one of claims 1-13 wherein the hydrocarbon conversion process is an alkylation process.

15. A process according to any one of claims 1-14 wherein the content of organic chlorides is reduced.

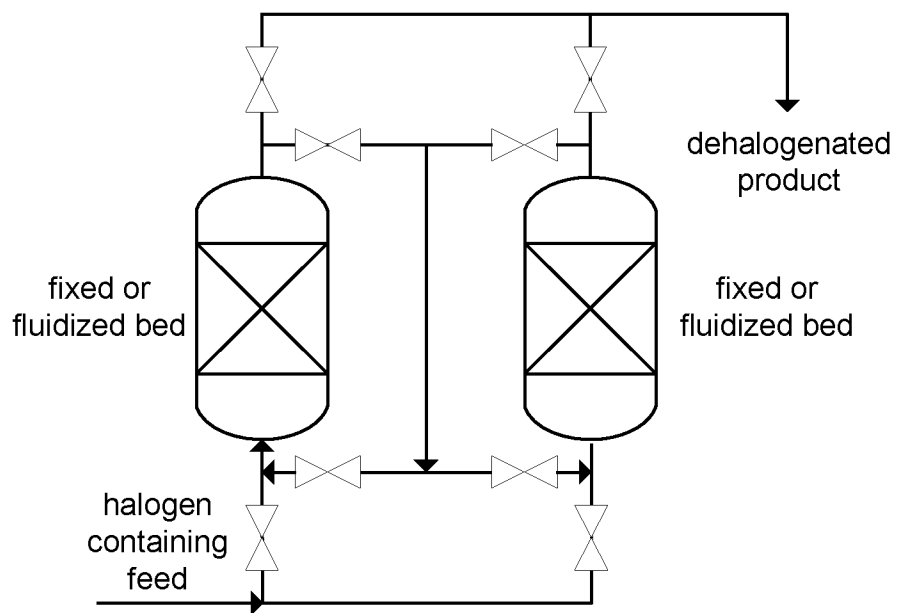


Fig 1

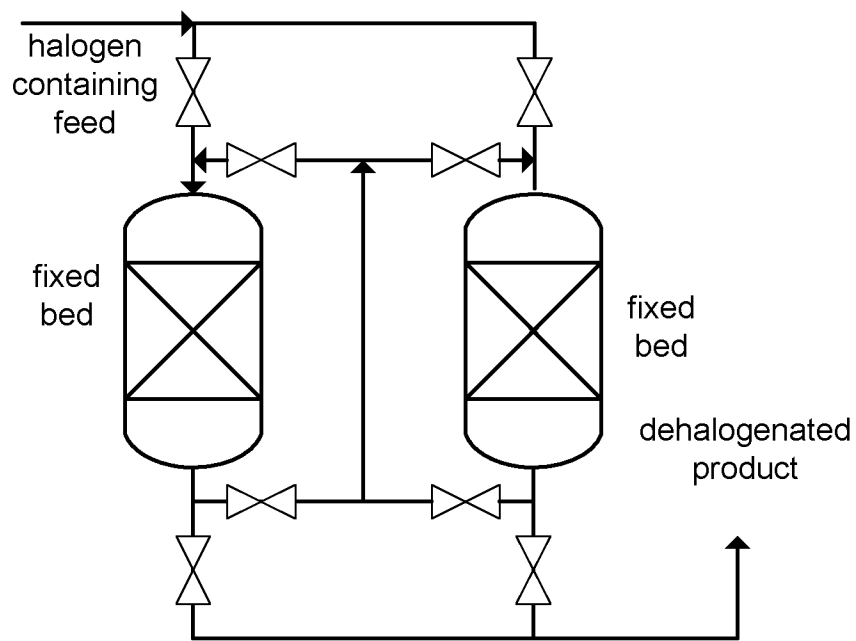


Fig 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/066483

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G19/067 C10G19/073 C10G29/04 C07C7/148
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/079107 A1 (CHEVRON USA INC [US]; DRIVER MICHAEL S [US]; LACHEEN HOWARD S [US]; H0) 25 June 2009 (2009-06-25) claim 1; examples 1-3 -----	1-15
X	US 2010/147746 A1 (DRIVER MICHAEL S [US] ET AL) 17 June 2010 (2010-06-17) cited in the application claims 1,4 -----	1-15
A	US 4 755 628 A (ADAMS EDWARD C [US]) 5 July 1988 (1988-07-05) the whole document -----	1-15
A	US 1 934 068 A (JOLLY EDWARD M ET AL) 7 November 1933 (1933-11-07) the whole document ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

20 October 2011

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31/10/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/066483

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MIYOSHI, NISHIO, YASUHURA, MORITA: "Dechlorination of hexachlorobiphenyl by using potassium-sodium alloy", CHEMOSPHERE, vol. 41, 2000, pages 819-824, XP002630013, the whole document -----	1-15
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A	US 5 928 500 A (RICHARD MICHAEL A [US] ET AL) 27 July 1999 (1999-07-27) the whole document -----	1-15
A	US 2009/264694 A1 (DRIVER MICHAEL S [US] ET AL) 22 October 2009 (2009-10-22) cited in the application the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/066483

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