

Declarations under Rule 4.17:

- *as to the identity of the inventor (Rule 4.17(i))*
- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

Title: Optimizing a MTA process

Since its discovery in the 1970's, zeolite catalyzed conversion of methanol to hydrocarbons has become increasingly important in the chemical industry and several variations of the process have been commercialized including MTO (methanol-to-olefins), MTP (methanol-to-propylene), and MTG (methanol-to-gasoline). Herein, the focus is on the MTA (methanol-to-aromatics) process, in which methanol is converted over a metal/oxide containing zeolite to a mixture of hydrocarbons with a high content of aromatic compounds.

In a first aspect of the present invention is provided a process which enables that the product from the MTA process, can be improved by increasing the reformat aromatic selectivity,

In a second aspect of the present invention is provided a process which enables that the product from the MTA process, can be improved without compromising the yield of aromatics.

These and other advantages are achieved by a process for producing hydrocarbons from a main feed comprising methanol and/or dimethyl ether (DME), said process comprising the steps of

- reacting a reaction feed over a bifunctional catalyst thereby obtaining a reaction effluent comprising aromatics,
- In a first separation, separating the reaction effluent into an aqueous phase, a first gas phase and a first liquid hydrocarbon phase,
- separating the first liquid hydrocarbon phase into at least an incondensable gas phase, one or more intermediate phases and an aromatic product phase,
- recycling at least part of the one or more intermediate phases, and
- the reaction feed comprises the main feed and the intermediate phase recycle.

In other words, by the present invention it is provided a process for producing aromatics from a feed comprising methanol (MTA). The process comprises an aromatics synthesis step (with one or more reactors in parallel) followed by more than one separation

steps from where is obtained one or more recycles of the one or more intermediate phases from the liquid hydrocarbon phase.

5 The first liquid hydrocarbon phase may comprise various aromatics such as benzene, toluene, xylenes, ethylbenzene, and heavier aromatic compounds with 9 or more carbon atoms, as well as paraffins, olefins, and naphthenes. Most of the hydrocarbons present in the first liquid hydrocarbon stream may be components with 4 or more carbon atoms, but this stream may also comprise lighter hydrocarbons in low concentrations. The first liquid hydrocarbon stream may also comprise small amounts of dissolved gases such as CO₂, CO, hydrocarbons with carbon number C1-C4, and H₂.

10 The aqueous condensate from the first separation comprises mainly water, but may also comprise small amounts of various oxygenates including methanol, other alcohols, aldehydes, and ketones as well as dissolved gases.

15 In the present MTA process, a main feed stream comprising methanol and/or DME (dimethyl ether) is preheated, mixed with one or more recycle streams and fed to the MTA reactor section.

20 The MTA conversion process may be carried out at a pressure of 5-60 bar, preferably 10-40 bar, at a temperature of 300-500°C, preferably 300-480°C, and a weight hourly space velocity (kg methanol and/or DME feed per kg of catalyst per hour) between 0.1 and 10, preferably 0.5-3.

25 Preferably the inlet temperature to the reactor is between 320°C and 380°C and the exit temperature is between 380°C and 480°C.

30 In case the MTA reactor is adiabatic, the difference between the outlet temperature and the inlet temperature is preferably between 30 and 150°C, more preferably between 50 and 130°C.

In case the MTA reactor is an adiabatic fixed bed reactor, the difference between the inlet temperature and the outlet temperature is preferably between 30 and 150°C, more

preferably between 50 and 130°C. Preferably the inlet temperature to the reactor is between 320°C and 380°C and the outlet temperature is between 380°C and 480°C.

5 In order to achieve a desired selectivity to aromatics, an MTA catalyst preferably comprises a zeolite or zeotype as well as a metal/oxide function. The zeolite/zeotype is responsible for conversion of oxygenates to hydrocarbons, while the metal/oxide function is responsible for dehydrogenation of intermediate hydrocarbons, e.g. dehydrogenation of naphthenes to aromatics and/or dehydrogenation of paraffins to olefins. The combination of a zeolite function and a dehydrogenation function is essential for achieving a
10 high yield of aromatics in the MTA process.

The yield of aromatics is defined as the amount (moles) of carbon in the produced aromatics divided by the amount (moles) of carbon in the oxygenates in the feed stream to the MTA reactor.

15 Different zeolite/zeotypes may be employed, including ZSM-5, ZSM-11, ZSM-23, ZSM-48, SAPO-34, however ZSM-5 may be preferred, since it has a suitable size selectivity to the desired methylated monocyclic aromatic species as well as a relatively low coking rate. The metal component of the MTA catalyst may in advantageous embodiments
20 be chosen from Zn, Ga, In, Ge, Ni, Mo, P, Ag, Sn, Pd and Pt or combinations thereof. Zn may be preferred over the other metals. Thus, a catalyst comprising Zn/ZSM-5 may be a particularly preferred catalyst system for the MTA process. Furthermore, the MTA catalyst may comprise phosphorus, which leads to better hydrothermal stability of the catalyst and thus longer ultimate catalyst lifetime.

25 It may be preferred to use a binder material in order to shape the catalyst. This binder material may be a normally employed binder material such as Al₂O₃, MgAl₂O₄, SiO₂, ZrO₂, TiO₂, MgO or mixtures thereof. Al₂O₃ may be preferred. If Al₂O₃ is used as binder, Zn may be present in the catalyst as ZnAl₂O₄. Similarly, if Al₂O₃ is used as
30 binder P may be present in the catalyst as AlPO₄.

An MTA catalyst may comprise 0.2 – 15 wt% Zn, or more preferably 3 – 15 wt% Zn or even more preferably 5 – 15 wt% Zn. Furthermore an MTA catalyst may comprise 0 – 10 wt% P, or more preferably 0.1 – 8 wt% P or even more preferably 0.5 – 5 wt% P.

The incondensable gas phase preferably comprises H₂, CO, CO₂, C₁-C₂. It may be desirable to recycle part of this stream to the MTA reactor, this is to act as a heat sink and/or to inhibit cocking. In case the stream of incondensable gasses is recycle to the MTA reactor, it may be preferable if the concentration of H₂ in the stream is low in order not to suppress the dehydrogenation activity of the MTA catalyst. Preferably the concentration of H₂ at the reactor inlet is less than 15 mol%, such as less than 10 mol% or more preferably less than 5 mol%, such as less than 1 mol%.

In one embodiment the aromatic product may arise from a split (distillation) of the first liquid hydrocarbon stream, done at conditions resulting in a distribution where benzene is preferentially found in the aromatic product phase rather than in the intermediate stream. Preferably, more than 70 wt% such as more than 80 wt% or more preferably more than 90 wt% of the benzene present in the first liquid hydrocarbon stream is retained in the aromatic product phase. A reformat product stream obtained in such a way is referred to as "C₆+".

In another embodiment, the split (distillation) of the first liquid hydrocarbon stream is done at conditions resulting in a distribution where toluene is preferentially found in the aromatic product phase rather than in the intermediate stream. Preferably, more than 70 wt% such as more than 80 wt% or more preferably more than 90 wt% of the toluene present in the first liquid hydrocarbon stream is retained in the aromatic product phase. A reformat product stream obtained in such a way is referred to as "C₇+".

In yet another embodiment, the split (distillation) of the first liquid hydrocarbon stream is done at conditions resulting in a distribution where xylenes are preferentially retained in the aromatic product phase rather than in the intermediate stream. Preferably, more than 70 wt% such as more than 80 wt% or more preferably more than 90 wt% of the xylene present in the first liquid hydrocarbon stream is retained in the aromatic product phase. A reformat product stream obtained in such a way is referred to as "C₈+".

Producing a C₆+ aromatic product stream may result in a higher yield of reformat than producing a C₇+ stream.

Producing a C7+ aromatic product stream may result in a higher concentration of aromatics in the reformat than producing a C6+ stream.

The intermediate phases comprise C3-C4 and/or C5, C5-C6 or C5-C7 depending on the desired composition of the aromatic product phase being C6+ or C7+ or C8+. The C5 fraction is defined in a way that C6+ hydrocarbons may be included (e.g. paraffins and/or olefins). The C5-C6 fraction is defined in a way that C7+ hydrocarbons may be included (e.g. paraffins and/or olefins). The C5-C7 fraction is defined in a way that C8+ hydrocarbons may be included (e.g. paraffins and/or olefins).

At least part of the intermediate phase is recycled. The intermediate phase may be split into two or more phases, for example into a fraction comprising C3-C4 (rich in propane and butane) and a fraction comprising reactants comprising C5, C5-C6 or C5-C7 (rich in paraffins and naphthenes).

In some embodiments at least part of fraction C3-C4 may be recycled to the main feed thereby forming the reaction feed. Recycling the C3-C4 stream may be beneficial since the concentration of H₂ in the reactor feed stream may be lowered as a consequence of recycling C3-C4, which may result in higher dehydrogenation activity of the MTA catalyst, and thus a higher yield of aromatics. Furthermore, the C3-C4 stream may contain olefins which will be converted if the stream is recycled to the MTA reactor. Propane and butanes are not very reactive, but may to a lesser extent be converted to aromatics (via dehydrogenation to olefins). Additionally, recycling the C3-C4 may allow reducing the total recycle gas for reactor temperature control because the C3-C4 fraction has a higher heat capacity than the first gas phase.

At least part of the fraction comprising reactants comprising C5, C5-C6 or C5-C7 may be recycled in order to utilize any reactants such as paraffins, olefins and/or naphthenes thereby increasing the aromatics yield. C5, C5-C6 or C5-C7 paraffins may also be converted to aromatics (via dehydrogenation to olefins). Generally paraffins are not very reactive under the reaction conditions in the MTA reactor, but longer (C5+) chained paraffins are more reactive than propane and butane, and some conversion of the C5+ paraffins is expected. On the other hand naphthenes are much easier to con-

vert to aromatics, particularly under reduced hydrogen partial pressure. Additionally, recycling the C5, C5-C6 or C5-C7 fraction may allow reducing the total recycle gas for reactor temperature control because the C5, C5-C6 or C5-C7 fraction has a higher heat capacity than the first gas phase. The C3-C4 fraction may be sold as LPG product, and it may be a possibility to recycle to the MTA reactor only the C5, C5-C6 or C5-C7 fractions.

The C3-C4 fraction as well as the fraction comprising reactants comprising C5, C5-C6 or C5-C7 may be essentially free of H₂ which makes the fraction comprising C3-C4 and the fraction comprising C5, C5-C6 or C5-C7 ideal as recycles. Low H₂ level in the recycle is advantageous as high H₂ levels in the reactor inlet may inhibit the dehydrogenation reactions and thus reducing the aromatic yield. Preferably, the hydrogen concentration at the gasoline reactor inlet should be less than 15 mol%, more preferably less than 10 mol% and even more preferably less than 5 mol%, such as less than 1 mol%.

At least part of the first gas phase from the first separator may also be used as recycle to the reactor. Alternatively or in combination, at least part of the first gas phase may be purged.

Depending on the degree of recycle of the first gas phase the first separator may be run to achieve specific compositions of the first gas phase.

Typically, if the first gas phase is recycled the first gas phase may preferably comprise H₂, CO, CO₂, C1-C4 hydrocarbons, which may be achieved by running the first separator at temperatures between 25 and 60°C, most preferably between 40 and 50°C and pressures between 10 and 30 bar, most preferably between 15 and 25 bar.

In case no or only a limited part of the first gas phase is recycled, the separation may preferably be conducted at higher pressure and/or lower temperature to increase the solubility of light hydrocarbons such as propane, propene, butanes and butenes in the first liquid phase.

In other advantageous embodiment of the invention, the flow of recycle gas from the first separator in the MTG loop to the inlet of the MTG reactor is low, in some embodiments even preferably 0 or close to 0, resulting in a low content of H₂ at the inlet to the MTG reactor. The low molar fraction of H₂ at the inlet of the MTG reactor may lead to high dehydrogenation activity of the MTG catalyst, and thus higher yield of aromatics. If there is no gas recycle from the first separator in the MTG loop, the temperature increase in the MTG reactor may be high, if too little recycle of one or more intermediate liquid phases is added to the feed stream.

10 I.e. by optimizing the ratio and content of the different recycles from the first gas phase as well as intermediate phases, it is possible to tune the reactor temperature as well as ensuring that the H₂ concentration is kept optimal and that useful reactants are recycled.

15 As the reaction feed is a combination of the main feed and one or more recycles, the reaction feed may comprise the feed stream as well as recycles of the C₃-C₄ fraction and/or the fraction comprising reactants comprising C₅, C₅-C₆ or C₅-C₇ and first gas phase.

20 Thus according to the present invention a variety of streams downstream the MTA reactor may be recycled to the MTA reactor whereby it is possible to optimize the MTA aromatic yield.

25 For example it is possible to cut the reformat in a C₇+ fraction which constitutes the product and recirculate at least part of the C₇- fraction back to the reactor. This has several potential benefits:

- The C₃-C₄ fraction comprises paraffins (e.g. propane, butane) that may be recycled to the MTA reactors reducing the H₂ molar fraction. In addition, light olefins (e.g. propene, butenes) are also found in this fraction and if recycled to the MTA reactors they may react to increase the yield of higher hydrocarbons, including aromatics.
- The C₅ fraction contains both pentanes and cyclopentanes, which are aromatics precursors.

• The C6 and C7 fraction is relatively poor in aromatics. These fractions mainly comprise paraffins as well as olefins and naphthenes. These fractions when being recycled to the MTA reactors are given an extra chance to react and produce more aromatics. Moreover, some of the compounds (e.g. paraffins) may also cumulate in the synthesis loop contributing to the reduction of H₂ molar fraction, favoring aromatization through dehydrogenation reactions. Some of the components typically found in the C5-C6 or C5-C7 fractions are olefins (e.g. 2-methyl-2-butene; 1-methyl-1-cyclopentene), paraffins (e.g. isopentane, 2-methylpentane), naphthenes (e.g. methylcyclopentane, methylcyclohexane).

Thus, the MTA process may be optimized by recycling of one or more streams downstream the MTA reactor. The MTA process may be optimized by:

- controlling recycle of the C3-C4 fraction as reactant and/or to adjust the hydrogen molar fraction in the MTA loop and/or
- controlling the recycle of the C5 or C5-C6 or C5-C7 fractions as reactant and/or for adjusting the hydrogen molar fraction in the MTA loop, and/or
- controlling the recycle of the first gas phase as reactant and/or for adjusting the hydrogen molar fraction in the MTA loop.

Figures 1 shows an example where a methanol containing feed (1) is warmed up and mixed with the recycle stream (6) and optionally with the stream (11b) into the reactor inlet stream (2). The reactor effluent (3) is cooled down and separated in a separator (14) into a water phase (7), a first liquid hydrocarbon phase (8) and a first gas phase (4). The first gas phase can be split into a purge (5) and the recycle stream (6). The first liquid hydrocarbon phase (8) is separated in a series of separation units (15), typically distillation columns, into an incondensable gas phase (9) comprising H₂, CO, CO₂, C1-C2 hydrocarbons, an intermediate phase comprising a C3-C4 fraction (stream 10a) comprising propane and/or butane, an intermediate phase comprising C5 or C5-C6 or C5-C7 hydrocarbon fractions (stream 11a, comprising paraffins, olefins and naphthenes) and a C6+ or C7+ or C8+ fraction, comprising aromatic compounds (stream 12). The intermediate phase (11a) can be mixed with, for example, the feed (1) as indicated by stream 11b or the recycle gas (6), etc. Optionally, at least part of the C3-C4 fraction can be combined to the C5 or C5-C6 or C5-C7 fraction, as indicated by dotted line (10b), constituting the intermediate phase.

Fig. 2 Shows an alternative wherein, at least part of the an intermediate phase comprising C3-C4 fraction (10c) and/or at least part of the intermediate phase comprising C5 or C5-C6 or C5-C7 fraction (11c) can be added at any point in the reactor, either as a simple mix or as a quench in between catalyst beds.

Figure 3 shows an exemplary MTA product (also called reformate) PIONA distribution (sorted according to carbon number) which shows that there are two main peaks: one around C4 (where paraffins are the main components) and another around C8 (where aromatics are the main components). It can be seen that cutting the reformate at around C6 or C7 would further increase its aromatic content at the expense of having an extra C5, C5-C6 or C5-C7 stream which would represent a reformate yield loss, but not necessarily an aromatic yield loss.

A process modification where at least part of the C5, C5-C6 or C5-C7 fraction is recirculated to the synthesis reactor is described herein. This entails that the paraffin rich stream (containing also olefins and naphthenes) has an extra chance to be converted over the MTA catalyst into aromatics (via dehydrogenation into olefins). In this way the reformate yield loss is limited since the only yield loss would be that of the paraffin dealkylation. Nonetheless the aromatics yield in the reformate is likely to increase by further reaction of the olefins, paraffins and/or naphthenes.

The overall result is an improvement in the reformate aromatic yield, making it a more valuable process than the standard MTA reformate.

Claims

1. Process for producing an aromatic rich hydrocarbon product from a main feed comprising methanol and/or DME, said process comprising the steps of
- reacting a reaction feed over a bifunctional catalyst thereby obtaining a reaction effluent comprising aromatics,
 - In a first separation, separating the reaction effluent into an aqueous phase, a first gas phase and a liquid hydrocarbon phase,
 - separating the liquid hydrocarbon phase into at least an incondensable gas phase, one or more intermediate phases and an aromatic product phase,
 - recycling at least part of the one or more intermediate phases, and wherein
 - the reaction feed comprises the main feed and the intermediate phase recycle.
2. Process according to claim 1, wherein the incondensable gas phase comprises H₂, CO, CO₂, C₁-C₂ hydrocarbons.
3. Process according to any of the preceding claims, wherein the aromatic product phase comprises C₆+ or C₇+ or C₈+ aromatic compounds.
4. Process according to any of the preceding claims, wherein the intermediate phases comprises C₃-C₄ hydrocarbons and at least a fraction comprising C₅ hydrocarbons, or C₅-C₆ hydrocarbons or C₅-C₇ hydrocarbons.
5. Process according to any of the preceding claims, wherein the one or more intermediate phases recycled is C₅ hydrocarbons
6. Process according to any of the preceding claims, wherein the one or more intermediate phases recycled is C₅-C₆ hydrocarbons
7. Process according to any of the preceding claims, wherein the one or more intermediate phases recycled is C₅-C₇ hydrocarbons
8. Process according to any of the preceding claims, wherein the intermediate phases comprises propane, propene, butane and/or butenes.

9. Process according to any of the preceding claims, wherein the intermediate phases comprises reactants with a carbon number of 5 or higher, comprising olefins, paraffins and/or naphthenes.
- 5 10. Process according to any of the preceding claims, wherein the first gas phase comprises H₂, CO, CO₂, C₁-C₄ hydrocarbons.
11. Process according to any of the preceding claims, wherein at least part of the first gas phase is purged
- 10 12. Process according to any of the preceding claims, wherein at least part of the first gas phase is recycled as part of the reaction feed, such as 10-100%, such as 15 – 95%, such as above 20% of the first gas phase is recycled as part of the reaction feed.
- 15 13. Process according to any of the preceding claims, wherein 0 – 10% of the first gas phase is recycled as part of the reaction feed, such as below 8% or below 5%, such as 0,1 – 5%, such as 0,5 – 2% or below 2% or below 1% of the first gas phase is recycled as part of the reaction feed.
- 20 14. Process according to any of the preceding claims, wherein at least part of one or more the intermediate phases is used to control the temperature in the MTA reactors by means of recycle.
- 25 15. Process according to any of the preceding claims, wherein the first separation is done in one or several separation and/or distillation operations
16. Process according to any of the preceding claims, wherein the feed stream comprising oxygenates is converted in the MTA reactor over a bifunctional catalyst comprising a zeolite and a dehydrogenation function (metal or oxide).
- 30 17. Process according to any of the preceding claims, wherein the feed stream comprising oxygenates is converted in the MTA reactor over a bifunctional catalyst comprising zeolite ZSM-5 and 0.2 – 15 wt% Zn, such as 3 – 15 wt% Zn or 5-15 wt% Zn.

18. Process according to any of the preceding claims, wherein the feed stream comprising oxygenates is converted in the MTA reactor over a bifunctional catalyst comprising zeolite ZSM-5, Zn and 0 – 10 wt% P, such as 0.1 – 8 wt% P or 0.5 – 5 wt% P.
19. Process according to any of the preceding claims, wherein the feed stream comprising oxygenates is converted in the MTA reactor over a bifunctional catalyst comprising zeolite ZSM-5 and Zn, where Al₂O₃ is used as binder to shape the catalyst.
20. Process according to any of the preceding claims, wherein the feed stream comprising oxygenates is converted over one or more beds of catalyst in one or more catalytic reactors
21. Process according to any of the preceding claims, wherein the feed stream comprising oxygenates is converted in one or more fixed bed reactors
22. Process according to any of the preceding claims, wherein the feed stream comprising oxygenates is converted in one or more fluid bed reactors
23. Method for optimizing a MTA process, by regulating the recycle of one or more recycles,
- controlling recycle of the C3-C4 fraction as reactant and/or to adjust the hydrogen molar fraction in the MTA loop and/or
 - controlling the recycle of the C5 or C5-C6 or C5-C7 fractions as reactant and/or for adjusting the hydrogen molar fraction in the MTA loop, and/or
 - controlling the recycle of the first gas phase as reactant and/or for adjusting the hydrogen molar fraction in the MTA loop.
24. A plant arranged to enable the optimization of an MTA process, said plant comprising
- means for providing a main feed
 - a reactor
 - a first separator
 - a separation section
 - means for
 - recycle and/or control the recycle of the C3-C4 fraction as reactant and/or to adjust the hydrogen molar fraction in the aromatics synthesis loop.

- 5
- recycle and/or control the recycle of the intermediate fraction as reactant and/or for adjusting the hydrogen molar fraction in the aromatics synthesis loop, and/or
 - recycle and/or control the recycle of the first gas phase as reactant and/or for adjusting the hydrogen molar fraction in the aromatics synthesis loop.

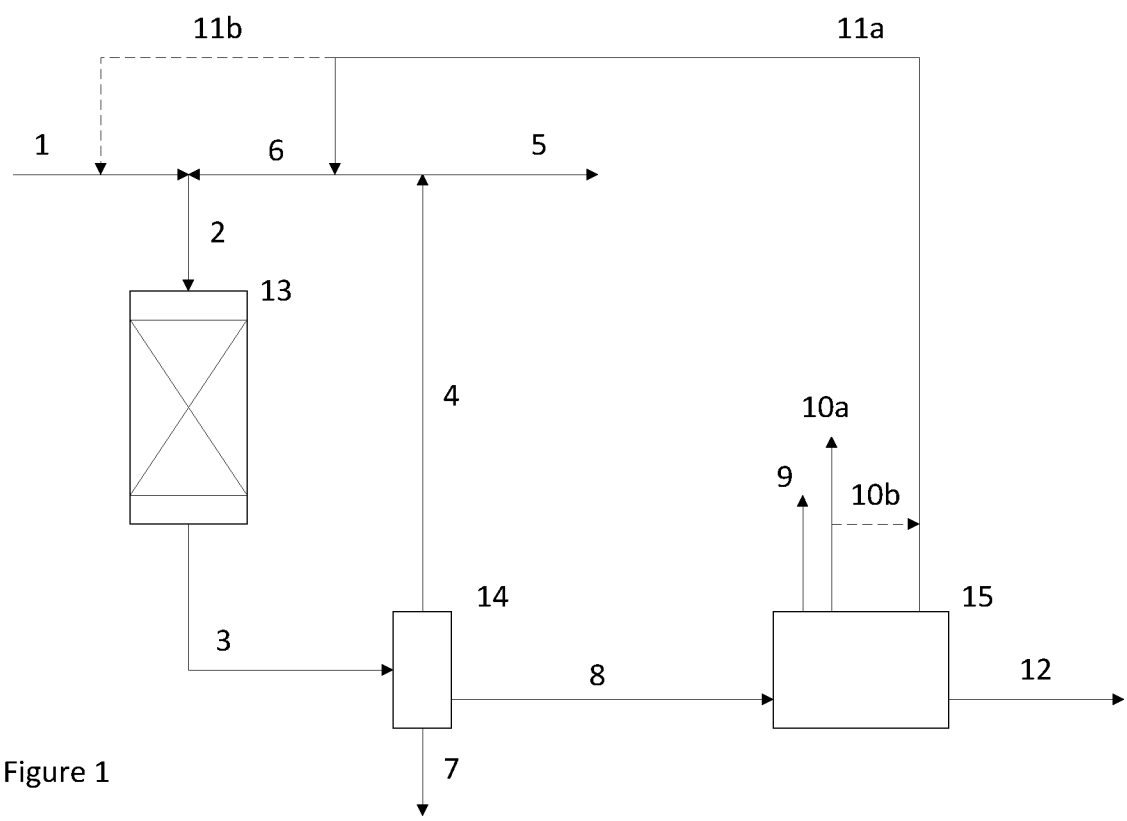


Figure 1

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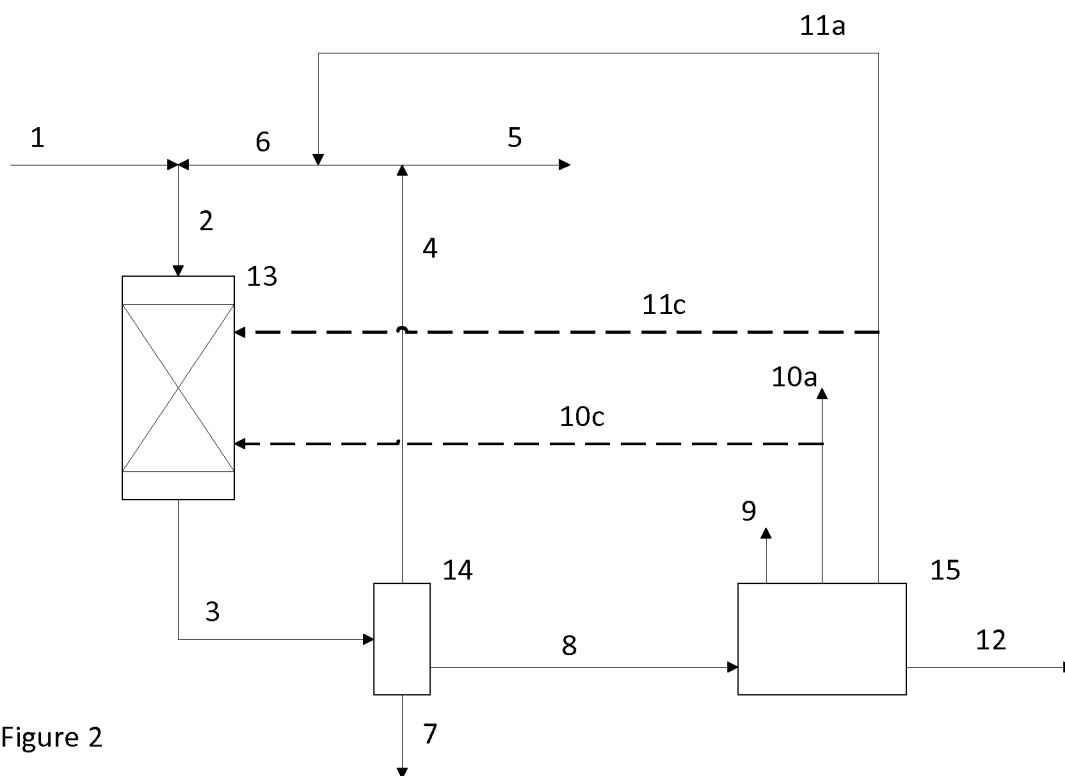


Figure 2

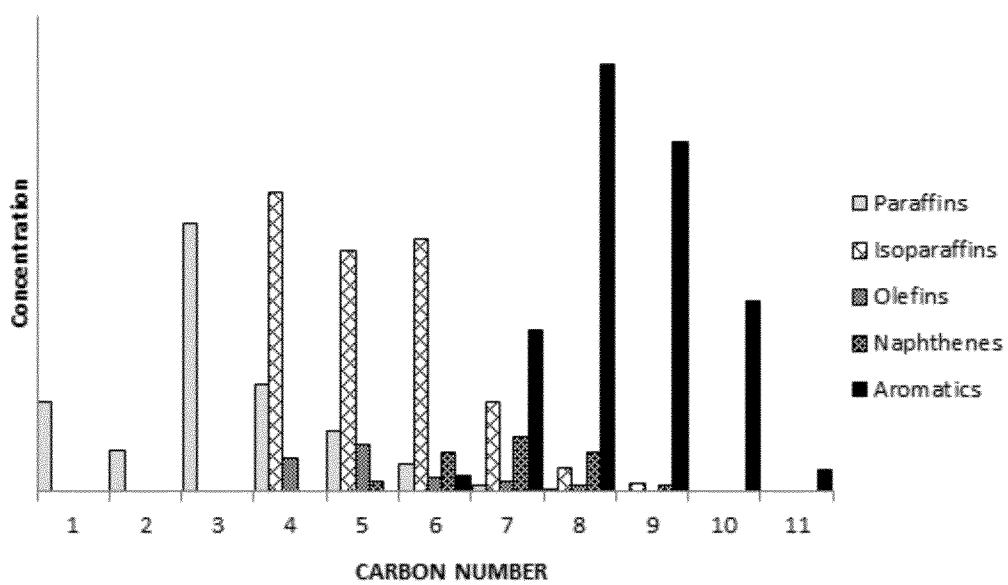


Figure 3

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/066866

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G3/00 C07C1/20 C07C15/02
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 practicable, 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.
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Y	abstract	16-19
X,P	& US 2017/145317 A1 (LISCHINER JOSEPH IZRAILEVICH [RU] ET AL) 25 May 2017 (2017-05-25)	1-15, 20-24
Y,P	paragraphs [0049], [0076]; figure 1	16-19
X	US 2014/018593 A1 (BIRKE GERHARD [DE] ET AL) 16 January 2014 (2014-01-16)	1-15, 20-24
Y	paragraphs [0015], [0068], [0069]; figure 2	16-19
X	US 4 709 113 A (HARANDI MOHSEN N [US] ET AL) 24 November 1987 (1987-11-24)	1-15, 20-24
Y	column 3, lines 24-65 column 7, line 20/21; figure 1	16-19
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

21 September 2017

Date of mailing of the international search report

28/09/2017

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/066866

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	----- US 2014/018592 A1 (CHEN XIQIANG [CN] ET AL) 16 January 2014 (2014-01-16) paragraph [0037]; claim 1; example 7 -----	16-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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