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 (72) Inventeurs/Inventors:
JOENSEN, FINN, DK;
MENTZEL, UFFE VIE, DK;
MENJON, IAN, DK
 (73) Propriétaire/Owner:
HALDOR TOPSOE A/S, DK
 (74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : REJET D'HYDROGENE DANS PROCEDE DE CONVERSION DE METHANOL EN HYDROCARBURE
 (54) Title: HYDROGEN REJECTION IN METHANOL TO HYDROCARBON PROCESS

(57) **Abrégé/Abstract:**

The present application relates to a process for production of hydrocarbons comprising the steps of - converting a feed stream comprising alcohols, ethers or mixtures hereof over a metal-containing zeolite based catalyst, active in dehydrogenation of hydrocarbons, in a conversion step thereby obtaining a conversion effluent, - separating said effluent to obtain an aqueous process condensate stream, a liquid hydrocarbon stream and a gaseous stream, - removing part of the hydrogen formed in the conversion step, and recycling at least part of the gaseous and/or liquid hydrocarbon stream to the conversion step.

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- (71) **Applicant:** HALDOR TOPSØE A/S [DK/DK]; Haldor
Topsøes Allé 1, 2800 Kgs. Lyngby (DK).
- (72) **Inventors:** JOENSEN, Finn; Møllevænget 28, 2970 Hør-
sholm (DK). MENTZEL, Uffe Vie; Apollovej 29B, 2720
Vanløse (DK). MENJON, Ian; Rønnegade 14, 5.TH, 2100
Copenhagen Ø (DK).
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Hydrogen rejection in methanol to hydrocarbon process

The conversion of methanol (MeOH) and/or dimethyl ether (DME), into hydrocarbon fuels and chemicals is of significant industrial importance. Prominent examples comprise methanol-to-gasoline (MTG) and methanol-to-olefins (MTO) processes.

In general, any alcohol and ether may be converted into hydrocarbons by these processes, but methanol is the preferred feedstock, because it may be produced in large scale and with high efficiency from any carbon-containing resource, such as coal, biomass, waste and natural gas. Prior to the conversion into hydrocarbons the methanol or alcohol feed may be converted, at least partially, into its ether analogue e.g. methanol to DME.

Similar processes have been disclosed for the conversion of alcohols into hydrocarbons, targeting different products such as aromatics.

The MTG process typically provides high-octane synthetic gasoline in excellent yields, close to about 90 per cent by weight of the total amount of hydrocarbons produced and with typical octane numbers close to 90, expressed in terms of $(R+M)/2$ (Research Octane Number (RON) + Motor Octane Number (MON)/2). The synthetic gasoline typically contains substantial amounts of aromatics which contribute significantly to the octane number. Even higher octane numbers may be obtained by increasing the aromatics content, e.g. by increasing the pressure or temperature in the gasoline synthesis reactor or by reducing the space velocity. Changing synthesis conditions to improve aromatics selectivity, and

thereby octane, however, imposes a penalty in terms of a reduced gasoline yield, because the formation of aromatics is inherently accompanied by increased selectivity to paraffins, in particular, propane and butanes which only to a limited extent may be added to the gasoline product slate due to their relatively high vapour pressures. In other words, the existing choice is between making a low-aromatics product in high yields or a high-aromatics product in low yields.

10

In a first aspect of the present invention is provided a process and plant for producing a hydrocarbon product with enhanced aromatics selectivity without simultaneously increasing the selectivity to light paraffins such as propane and butanes.

15

In a second aspect of the present invention is provided a process for making a highly aromatic product.

20

These and other advantages are provided by a process for production of hydrocarbons comprising the steps of

- converting a feed stream comprising alcohols, ethers or mixtures hereof over a metal-containing zeolite based catalyst, active in dehydrogenation of hydrocarbons, in a conversion step thereby obtaining a conversion effluent,
- separating said effluent to obtain an aqueous process condensate stream, a liquid hydrocarbon stream and a gaseous stream,
- removing part of the hydrogen formed in the conversion step, and

recycling at least part of the gaseous and/or liquid hydrocarbon stream to the conversion step.

30

I.e. according to the present invention there is provided a process for making a hydrocarbon product in which hydrogen produced in the conversion step is removed or partially removed from the synthesis loop, either by purging part of the gaseous recycle stream, hereinafter referred to as passive H₂ rejection, or by removing, partially or completely, H₂ from one or more recycle streams, hereinafter referred to as active H₂ rejection, in order to provide an at least partly H₂ depleted recycle. In the process e.g. methanol is converted over a preferably acidic zeolite based catalyst, combined with a metal or metal oxide component active in the dehydrogenation of hydrocarbons, into a conversion effluent comprising aromatics.

Where an at least partly H₂ depleted recycle is obtained the present is a process for production of hydrocarbons comprising the steps of

- converting a feed stream comprising alcohols, ethers or mixtures hereof over a metal-containing zeolite based catalyst, active in dehydrogenation of hydrocarbons, in a conversion step thereby obtaining a conversion effluent,
- separating said effluent to obtain an aqueous process condensate stream, a liquid hydrocarbon stream and a gaseous stream,
- removing part of the hydrogen formed in the conversion step,
- obtaining an at least partly H₂ depleted recycle stream,
- recycling at least part of the at least partly H₂ depleted recycle stream, the gaseous and/or liquid hydrocarbon streams to the conversion step.

The conversion effluent is separated into a gaseous stream, an aqueous process condensate and a liquid hydrocarbon stream comprising a hydrocarbon product.

5 By the present process and plant wherein hydrogen is removed it is thus possible to increase the aromatics selectivity and at the same time reduce the selectivity to light paraffins, such as propane and butanes.

10

Methanol to aromatics

The obtained hydrocarbon stream may be rich in aromatics, in which case the process hereinafter is referred to as a methanol-to-aromatics (MTA) process.

15

In the MTA conversion process methanol is converted into aromatics while dehydrogenation of hydrocarbons including one or more types of hydrocarbons, comprising naphthenes, paraffins and isoparaffins, into olefins and/or aromatics
20 is taking place.

The MTA conversion process may preferably be carried out at a pressure 5-60 bar, preferably 10-40 bar, temperature 300-500°C, preferably 330-480°C and/or weight hourly space velocities (kg alcohol and/or ether feed per kg of catalyst
25 per hour) between 0.1 and 10 preferably 0.3-3.

The MTA process may provide a product particularly suited as feedstock for downstream aromatics processing, e.g. for
30 making para-xylene.

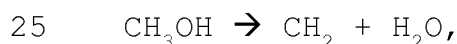
Methanol to gasoline

The obtained hydrocarbon stream from the present process may comprise raw gasoline, in which case the process hereinafter is referred to as a methanol-to-gasoline (MTG) process.

In the MTG conversion process methanol is converted into a raw gasoline comprising aromatics, naphthenes, paraffins and isoparaffins and olefins while dehydrogenation of hydrocarbons including one or more types of hydrocarbons, comprising naphthenes, paraffins and isoparaffins, into olefins and/or aromatics is taking place.

The MTG conversion process may preferably be carried out at a pressure 5-60 bar, preferably 10-40 bar, temperature 300-500°C, preferably 300-430°C and weight hourly space velocities (kg alcohol and/or ether feed per kg of catalyst per hour) between 0.1 and 10 preferably 0.5-3.

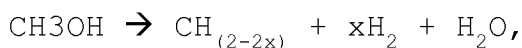
In other words, the traditional methanol-to-hydrocarbons reactions (MTG and MTO) may overall be formulated as a mere dehydration of methanol, forming hydrocarbons and water:



where CH_2 denotes the average sum formula of the entire hydrocarbon product. Thus, the overall molar hydrogen-to-carbon ratio of the entire hydrocarbon product is two: $\text{H/C} = 2$. Some of the product hydrocarbons, aromatics, have H/C ratios below 2, paraffins and isoparaffins have H/C ratios

above 2, whereas olefins and naphthenes both have H/C equal to 2.

As opposed to such traditional methanol-to - hydrocarbons
5 reactions (MTG and MTO) this invention provides a hydrocarbon product which has an overall H/C ratio of less than two, according to



10

thereby forming more aromatics on the expense of n- and i-paraffins, in particular, light n- and i-paraffins, such as ethane, propane and butanes, and providing a highly aromatic hydrocarbon product.

15

The obtained hydrocarbon product of the present invention may be rich in aromatics and provide useful as feed or aromatics processing, as blendstock, e.g. similar to reformate, in refineries, or the product or part of the product
20 may be upgraded by conventional means to provide a finished gasoline product.

Hydrogen rejection

The dehydrogenation reaction, promoting the formation of
25 aromatics, is equilibrium-limited and in a synthesis loop, hydrogen may build up until the dehydrogenation reaction becomes essentially extinct.

Therefore, removal of hydrogen from the loop ensures that
30 the dehydrogenation reaction is sustained. The hydrogen removal may be continuous, carried out in intervals and/or determined by preselected or adapted desired H₂ concentra-

tions e.g. in depleted or partially depleted recycle stream(s).

5 According to the invention H₂ may be at least partly removed by one or more methods removing H₂ at one or more stages, from one or more streams.

10 As mentioned above, removal of H₂ from the synthesis loop may be passive, i.e. by purging part of the gaseous recycle stream, or active, to be understood as methods by which one or more recycle streams are selectively depleted or partially depleted with respect to H₂.

15 Depending on the method used for H₂ removal more or less H₂ may be removed. Also, the selectivity in the removal towards H₂ may vary. For example if a permselective membrane is used for the removal the membrane may allow other substances than H₂ such as methane and carbon monoxide to pass through in which case not only H₂ is removed. Similarly
20 e.g. oxidation steps may result in oxidation of other substances than H₂, e.g. carbon monoxide.

25 According to some embodiments an at least partially H₂ depleted recycle stream is obtained from the gaseous stream by passing the gaseous stream to a hydrogen permselective membrane. I.e. the gaseous stream is provided to a stage wherein the gas is passed to a membrane removing H₂. The permeation of H₂ in the selective membrane may be adjusted to leave a pre-determined amount of hydrogen in the retentate recycled to the conversion step as the at least partially
30 H₂ depleted recycle stream.

Alternatively, the at least partially H₂ depleted recycle stream is obtained from the gaseous stream by passing said gaseous phase, after admixture with a predetermined amount of dioxygen, to a catalytic preferential oxidation, commonly known as PrOx, step where hydrogen is reacted with said predetermined amount of oxygen to form water and recycling said reacted stream, at least partially depleted in hydrogen, to the conversion step. The catalytic oxidation is preferably carried out at essentially the same pressure as in the conversion step at a temperature between 50 and 300°C, preferably, 100-200°C. Catalysts effective in selective oxidation typically comprise a noble metal supported on an inorganic metal oxide.

Optionally, the at least partially H₂ depleted recycle stream is obtained from the gaseous stream by passing said gaseous phase, after admixture with a predetermined amount of a non-dioxygen hydrogen scavenger, to a catalytic oxidation step where hydrogen is reacted with said predetermined amount oxidizing agent and recycling said reacted stream, at least partly depleted in hydrogen, to the conversion step.

The hydrogen scavenger may be an aldehyde or a ketone, in which case said aldehyde and hydrogen is converted into an alcohol over a hydrogenation catalyst. For example, the aldehyde may be formaldehyde in which case formaldehyde and hydrogen is converted into methanol over a hydrogenation catalyst.

The hydrogen scavenger may be hydrogen peroxide in which case hydrogen peroxide and hydrogen is converted into water over a hydrogenation catalyst.

- 5 The hydrogen scavenger may be carbon oxides, CO and/or CO₂ in which case carbon oxides are converted into methane over a methanation catalyst.

10 The separation step, where the effluent from the conversion step is separated into a gas phase and aqueous and hydrocarbon liquid phases, is typically conducted by cooling the conversion effluent essentially at the synthesis pressure, at 10-50 bar, typically by cooling to a temperature between 30 and 80°C. Under these conditions H₂ is almost only found
15 in the gaseous phase in the separator, and the liquid hydrocarbon (as well as the aqueous phase) is almost completely H₂ free. This means that the liquid hydrocarbon phase may be separated into a product phase and one or more lower- and/or higher-boiling phases, and at least one of
20 the lower- and/or higher-boiling phases can then at least partially be recycled to the conversion step as one of one or more at least partially H₂ depleted recycle.

25 Thus, several embodiments according to the present invention are proposed, wherein hydrogen may be removed from the synthesis loop and thereby enhance the selectivity to aromatics. Other means of promoting the selectivity to aromatics for example includes increasing the temperature and/or reducing the pressure in the conversion reactor, thereby
30 thermodynamically favouring the dehydrogenation reaction and, in turn, enhancing the selectivity to aromatics.

The degree of H₂ removal affects the products from the conversion. As mentioned above, if no means of hydrogen removal is established, hydrogen will accumulate in the loop and, eventually, the dehydrogenation reaction will cease.

5 Therefore, continuous removal of hydrogen from the loop may be required in order to sustain the dehydrogenation reaction. To which extent yield and selectivity may be increased depends on how much hydrogen is rejected from the synthesis loop. Thus, if only a limited part of the hydro-

10 gen is rejected, e.g. purging part of the recycle gas (passive rejection) this will lead to a product with a slight enrichment in aromatics, whereas a high degree of hydrogen rejection, as may be achieved by active H₂ rejection as described above, will provide a product with a high aromatics

15 content and even with aromatics as the main constituent.

The extent of hydrogen removal, therefore, represents a convenient and efficient tool for controlling aromatics selectivity and product yield. Thus, the more hydrogen is re-

20 jected from the synthesis loop, the more room is left for the dehydrogenation reaction to take place in the conversion reactor. Preferably, a high rate of rejection of hydrogen is desired in order to maximize the yield of aromatics.

25

In a methanol-to-gasoline context removal of hydrogen, passive or active, will lead to a higher gasoline yield as

30 well as improved octane due the enhanced selectivity to aromatics. However, in most areas the aromatics content is regulated, typically to 35 vol% (some 40 wt%), which impos-

es a limit to how much hydrogen may be removed. Nonetheless, a few per cent improvement in gasoline yield and at the same time gaining a few numbers in octane represents a significant economic advantage. Moreover, as will be shown
5 by examples, the selectivity to heavy oil (carbon number C11 and higher) and durene (1,2,4,5 tetramethylbenzene) is significantly reduced by the present process. I.e. the invention provides for making gasoline with improved yield and octane and with reduced selectivity to heavy oil and
10 durene.

In an MTA context, there is no limit as to how much hydrogen should be removed and aromatic yields in the order of 70% or more may be achieved at close to complete hydrogen
15 rejection.

The selectivity to aromatics increases with temperature, in part due to higher rates of reaction, but primarily, because dehydrogenation becomes favoured thermodynamically by
20 an increase in temperature. Consequently, higher aromatic yields may be obtained by conducting the conversion at higher temperatures.

Thus the present process and plant provides a method for
25 making hydrocarbons wherein the content of aromatics in the product slate may be controlled to a significant extent by applying a catalyst or a combination of catalysts active in dehydrogenation and methanol-to-hydrocarbons formation and a means of passive or active rejection of hydrogen from the
30 synthesis loop, the degree of which passive and/or active, controls the amount of aromatics in the product slate.

The feed stream may comprise methanol, dimethyl ether or mixtures hereof.

5 In preferred embodiments the process is carried out in either a fixed bed or a fluid bed reactor.

The present invention also relates to a plant for the conversion of methanol to hydrocarbons comprising aromatics, said plant comprising

- 10 - means for supplying a feed stream comprising methanol,
- a conversion reactor
- a separator for separating a conversion effluent into a gaseous recycle stream, process condensate and a liquid product, and
- 15 means for removing H₂ from the synthesis loop by purging part of the gaseous recycle stream, and/or by reducing the hydrogen concentration in at least part of the effluent thereby obtaining at least one at least partly H₂ depleted recycle stream.

20

As discussed above in relation to the process the plant may advantageously comprise means for removing H₂ from the recycle stream. The means for removing H₂ from the recycle stream may be, e.g., a selective membrane, a preferential

25 oxidation (PrOx) and/or a step wherein a hydrogen scavenger is admixed into the recycle stream and reacted with hydrogen. Preferred scavengers comprise aldehydes, ketones, hydrogen peroxide or carbon oxides, reacting with hydrogen

30 hols, water or methane, respectively.

I.e. the H₂ may be removed by various means. In the simplest way, H₂ may be removed by purging part of the gaseous recycle stream. This may to some extent improve the yield of aromatics, and C₅₊ yield and selectivity to aromatics and may, e.g. in an MTG process, be exploited to improve gasoline yield and octane number. However, when the desired product is aromatics, a simple purge may not be sufficient to provide an aromatics selectivity high enough to make an aromatics process economically justifiable, even given the benefit of operating at higher temperature. Therefore, additional means of improving aromatics selectivity may be preferred involving active rejection of hydrogen from the synthesis loop by one or more of the methods described above.

15

Where a hydrogen scavenger such as formaldehyde is converted into methanol in the presence of H₂ and a hydrogenation catalyst the plant may further comprise a hydrogenation reactor wherein a hydrogen scavenger is converted into methanol in the presence of H₂ and a hydrogenation catalyst. The same applies to other hydrogen scavengers, such as hydrogen peroxide, converting into water by reaction with hydrogen. Also, as mentioned above, excess hydrogen may be removed through methanation, converting CO and/or CO₂ and hydrogen into methane.

20
25

A setup with a PrOx may provide the option of regulating the H₂ removal from 0-100%. In the PrOx reactor the H₂ removal may be controlled by controlling the O₂ flow rate to the PrOx reactor. A suitable PrOx catalyst may typically consist of a noble metal or a mixture of noble metals such as Pt, PtSn In Pd, or Ru, supported on an oxidic carrier

30

such as alumina. Typical reaction conditions are 100-300°C and the pressure may be adapted to the pressure in the synthesis loop.

5 Removal of hydrogen in gas streams by permselective membranes is a well-known technology, applied commercially and offered by a number of providers, e.g. Air Products, UOP and MTR Inc. Typically, the degree of hydrogen removal is determined by the pressure and the hydrogen concentration
10 of the hydrogen-containing gas stream and the effective membrane area is determining for how much hydrogen can be removed. As mentioned above, other substances than H₂ such as methane and carbon monoxide will to some extent permeate the membrane.

15 Thus, where H₂ is removed from the gas stream from the separator the means for removing H₂ from at least part of the effluent obtaining at least one at least partly H₂ depleted recycle stream may be a selective membrane, a PrOx and/or a
20 step wherein a hydrogen scavenger, typically formaldehyde, hydrogen peroxide or carbon oxides are converted into methanol, water or methane, respectively, in the presence of H₂ and a hydrogenation catalyst.

25 The means for removing H₂ from at least part of the effluent obtaining at least one at least partly H₂ depleted recycle stream may also, or alternatively, comprise means for separating the liquid hydrocarbon stream into at least a product phase and one or more lower- and/or higher-boiling
30 phases and means for recycling at least one of said lower- and/or higher-boiling phases as the at least partly H₂ depleted recycle. Thus, the plant may comprise a second sepa-

rator (or one or more additional separators) wherein the liquid hydrocarbon stream is separated into at least two fractions e.g. C₃-C₄ and a C₅₊ fraction. As the liquid hydrocarbon stream may contain H₂ to a very limited degree (as H₂ is present in gas phase in the first separator) at least part of the C₃ - C₄ stream may be used a H₂ depleted recycle. From the second or one or more additional separators e.g. a light fraction comprising H₂ from the liquid hydrocarbon stream, CH₄, Co and/or CO₂ may also be obtained.

10

Catalysts

The catalysts applied in relation to this invention in general comprise an acidic component in the form of a microporous catalyst, e.g. in the form of a zeolite (e.g. ZSM-5, ZSM-11 or ZSM-48) or a zeotype (e.g. a silicoaluminum phosphate) and a metal component, selected from the group of Zn, Ga, In, Ge, Ni, Mo, P, Ag, Sn, Pd and Pt. Also mixtures of two or more metals or metal oxide may be applied, e.g., Pt-Sn, which is known as an efficient dehydrogenation catalyst.

20

Various methods may be applied to produce the catalyst: The two components may constitute an integrated entity, e.g. as obtained by introducing the metal component by impregnation or ion-exchange to the zeolite, either onto the zeolite itself or onto an extrudate in which the zeolite is embedded in a binder matrix, e.g. alumina. The metal component may also be added in the form of a salt or an oxide, together with binders or lubricants during fabrication of the acid component, e.g. during extrusion or pelletization.

30

Also physical mixtures of several acidic and metal components may be applied and the mixture may be charged to the reactor to form a uniform mixture or to form alternating layers or they may be graded to various degrees.

5

If the zeolite catalyst is a single bifunctional catalyst active towards both methanol to hydrocarbons and dehydrogenation, only one catalyst may be needed in the process.

10 In several embodiments of the present invention the acidic zeolite catalyst comprises metal and/or metal oxide in combination with a zeolite, e.g. H-ZSM-5.

The applicant has shown that, quite surprisingly, even at
15 mild reaction conditions, a bifunctional catalyst comprising Zn and H-ZSM-5 i.e. a Zn/ZSM-5 catalyst shows significant selectivity to aromatics. The applicant also surprisingly found that using the incorporation of Zn into the acidic zeolite catalyst provided a hydrocarbon product with
20 less durene. Durene (1,2,4,5-tetramethylbenzene) is a component that is formed in appreciable amounts in the methanol-to-gasoline process, typically in the range from 4-8 wt% in the gasoline product. Due to its high melting point (79°C) durene may cause plugging of the engine's fuel injection system in cold weather. Therefore, normal practice in synthetic gasoline manufacture involves a separate process step to reduce the amount of durene by hydroisomerization and dealkylation to provide a final gasoline with a
25 durene content of less than about 4 wt% at which level
30 durene has no negative impact on driveability. Therefore, reduced selectivity to durene is advantageous. The applicant also found that the zinc-containing catalyst showed a

reduced selectivity to hydrocarbons with carbon numbers higher than C11, commonly referred to as heavy oil, which causes the end boiling point of the gasoline product to increase and, therefore, must be removed from the gasoline product in order to meet gasoline specifications, thereby representing a loss of gasoline product.

Examples

The following examples demonstrating the benefits of using a combination a Zn dopant and H-ZSM-5. It will be understood that the combination of H-ZSM-5 or other zeolites or zeotypes in combination with other metals or metal oxides capable of dehydrogenation of hydrocarbons may lead to similar effects as regards hydrocarbon yields and selectivities.

Catalyst preparation

Catalysts applied in the examples were prepared by extrusion of H-ZSM-5 (CBV-8014 obtained from Zeolyst International and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 80) with an alumina binder material in the proportion of 65 wt% of H-ZSM-5 and 35 wt% alumina binder, adding water to obtain a paste and extruding the paste through a die with a diameter of 1.4 mm. The extrudates were subsequently dried in air at 120°C and calcined in air at 500°C for four hours.

Samples of calcined extrudates were then impregnated with an aqueous solution of zinc nitrate: 40 g of extrudates was impregnated with a solution of 5.46 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 25 ml of de-ionized water. The impregnated extrudates were dried
5 overnight at 110°C and finally calcined in air at 500°C for 4 hours to obtain a catalyst containing 2.9 wt% Zn. A similar catalyst with a higher zinc loading of 9.6 wt% was prepared following the same procedure, but applying an impregnation solution of 20.7 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 25 ml
10 of de-ionized water.

Example 1-2

In a reference experiment (example 1) applying a typical
15 MTG catalyst, a microreactor consisting of a 2 mm inner diameter isothermal reactor was charged with 0.10 g of H-ZSM-5 extrudates. The reactor was heated in an oven to 370°C and pressurized to 20 bar g and the catalyst was contacted with a feed of 6.6 mol% methanol (balanced by nitrogen) at
20 a weight hourly space velocity, WHSV (g methanol per g catalyst per hour) of 2.0.

Another experiment (example 2) was conducted under same conditions, using the same catalyst amount as above, but
25 this time applying a Zn-impregnated catalyst containing 2.9 wt% zinc.

Results of the two experiments, averaging a test period of 30 hours are shown in Table 1.

Table 1

Example	1	2
Temperature (°C)	370	370
Pressure (bar g)	20	20
WHSV	2.00	2.00
Products (wt% of total HC)		
n-paraffins	17.64	11.27
i-paraffins	35.13	30.39
Olefins	8.51	15.55
Naphthenes	2.43	2.97
Aromatics	35.06	39.06
C11+ ("heavy oil")	0.89	0.50
Propane and butanes	31.84	20.62
Overall molar H/C ratio in hydrocarbon product	2.00	1.90
Overall C5+ yield	60.27	66.26
Aromatics in C5+ fraction	58.20	58.93
Olefins in C5+ fraction	3.38	5.49
Durene in C5+ fraction	8.36	6.51

By comparison, example 1 and 2 show that the Zn-containing catalyst provides a C5+ yield (wt% C5+ of total hydrocarbon fraction) higher than the reference catalyst, a higher yield of aromatics and olefins, a reduced selectivity to C11+ ("heavy oil") and a reduced selectivity to durene. Also, the overall molar hydrogen-to-carbon (H/C) ratio of the hydrocarbon product is reduced when zinc is added to the catalyst, indicating that dehydrogenation (liberation as H₂) takes place over the catalyst, while the Zn-free catalyst provides a hydrocarbon product with a H/C ratio of 2.00, as expected from the mere dehydration of methanol.

Example 3

The experiment of example 2 was repeated, with the only difference that in this the catalyst impregnated with 9.6 wt% zinc was applied.

5

Results of the experiment, averaging a period of 30 hours are shown in Table 2 and compared with the result of example 2.

10 Table 2

Example	2	3
Temperature (°C)	370	370
Pressure (bar g)	20	20
WHSV	2.00	2.00
Products (wt% of total HC)		
n-paraffins	11.27	9.10
i-paraffins	30.39	31.80
Olefins	15.55	13.47
Naphthenes	2.97	3.09
Aromatics	39.06	42.01
C11+ ("heavy oil")	0.50	0.32
Propane and butanes	20.62	17.94
Overall molar H/C ratio in hydrocarbon product	1.90	1.87
Overall C5+ yield	66.26	70.69
Aromatics in C5+ fraction	58.93	59.44
Olefins in C5+ fraction	5.49	4.89
Durene in C5+ fraction	6.51	6.98

Example 3 demonstrates that the incorporation of additional zinc leads to a further increase in the yield of aromatics and C5+ hydrocarbons and a further reduction in the selectivity to "heavy oil". Incorporation of additional Zn to

15

the catalyst is also reflected by a further decrease in the H/C ratio.

Example 4

5 Examples 1-3 demonstrate that incorporation of Zn onto the catalyst provides higher aromatic yield and higher C5+ yield, whereas the amount of aromatics in the C5+ fraction remains essentially constant. This following example shows the effect of increasing the temperature in the reactor:
 10 The experiment of example 3 was repeated using the same catalyst, except that the temperature was increased to 420°C.

Results of this experiment, averaging a period of 30 hours
 15 are reported in Table 3 and compared with the result of example 3.

Table 3

Example	3	4
Temperature (°C)	370	420
Pressure (bar g)	20	20
WHSV	2.00	2.00
Products (wt% of total HC)		
n-paraffins	9.10	13.62
i-paraffins	31.80	20.32
Olefins	13.47	8.11
Naphthenes	3.09	1.73
Aromatics	42.01	55.92
C11+ ("heavy oil")	0.32	0.63
Propane and butanes	17.94	18.59
Overall molar H/C ratio in	1.87	1.76

hydrocarbon product		
Overall C5+ yield	70.69	70.66
Aromatics in C5+ fraction	59.44	79.12
Olefins in C5+ fraction	4.89	1.39
Durene in C5+ fraction	6.98	1.65

Example 4 demonstrates that, by increasing the temperature, the selectivity towards aromatics is significantly enhanced, from about 42 wt% to about 56wt% of the total hydrocarbon fraction, and the C5+ fraction becomes substantially richer in aromatics. Also the amount of heavier aromatics, such as durene, is significantly reduced and the overall H/C ratio is significantly reduced as well.

10 Examples 5-7

Examples 5-7 demonstrate the influence of hydrogen on yield and selectivity. A reference experiment with un-doped H-ZSM-5 (example 5) was conducted at 420°C and a weight hourly space velocity of 1.6. Example 5 was then repeated, except that the same Zn-doped catalyst as applied in example 2 was applied (example 6). Finally, example 6 was repeated, but this time the nitrogen carrier gas was replaced by a mixture of 5 vol% hydrogen in nitrogen (example 7).

20 The results of the three experiments, averaging a period of 30 hours are reported in Table 4.

25

Table 4

Example	5	6	7
Temperature (°C)	420	420	420
Pressure (bar g)	20	20	20
WHSV	1.6	1.6	1.6
Carrier gas (vol% H ₂ /N ₂)	0/100	0/100	5/95
Average over period (hrs)	0-30	0-30	0-30
Products (wt% of total HC)			
n-paraffins	27.30	12.45	14.31
i-paraffins	27.86	24.52	29.89
Olefins	7.92	13.79	9.04
Naphthenes	1.30	2.56	2.94
Aromatics	35.18	46.50	43.72
C11+ ("heavy oil")	0.61	0.58	0.38
Propane and butanes	39.33	19.11	23.20
Overall molar H/C ratio in hydrocarbon product	2.01	1.83	1.89
Overall C5+ yield	50.50	66.99	65.98
Aromatics in C5+ fraction	69.91	69.38	66.25
Olefins in C5+ fraction	1.76	3.76	2.11
Durene in C5+ fraction	1.48	2.54	1.96

By comparing example 6 with reference example 5 it is again shown that incorporation of Zn to the H-ZSM-5 catalyst leads to a significant improvement in yield and aromatics selectivity. The effect of hydrogen at the inlet of the reactor is demonstrated by comparing example 6 and 7, showing that the presence of hydrogen causes a decline in the aromatics selectivity and a slight reduction in the C₅₊ yield. However, when comparing example 7 with reference example 5 it is clear that, despite the presence of hydrogen, the C₅₊

yield and aromatics selectivity is still significantly higher, showing that the Zn-doped catalyst is capable of improving yield and aromatics selectivity even when hydrogen is present at the reactor inlet. This demonstrates
5 that, in a synthesis loop, controlling the amount of hydrogen recycled to the conversion reactor inlet provides a means of directing the selectivity towards aromatics.

It is also observed (example 6 & 7) that the presence of
10 hydrogen reduces the formation of durene and heavy oil. At the high temperatures applied in examples 5-7 some increase in durene levels are observed when applying the Zn-doped catalysts relative to the un-doped catalyst. However, in these examples durene selectivity are already so low (below
15 4 wt%) that it is without any significance to driveability. In conclusion, examples 5-7 show that the incorporation of Zn to the zeolite increases the aromatics selectivity and the C₅₊ yield, even so in the presence of hydrogen in the feed and that the presence of hydrogen in the feed leads to
20 a reduction in the formation of durene and heavy oil. Thus, in a synthesis loop, finite amounts of hydrogen in the recycle stream is not necessarily prohibitive in regard to achieving the desired effects according to the present invention, namely that of increasing C₅₊ yield and aromatics.

25
In the following the process and plant is further described with reference to the accompanying drawings. The drawings show exemplary embodiments of the present process and plant and are not to be construed as limiting to the scope of the
30 present application.

Fig. 1 shows a schematic setup of a first embodiment according to the present invention;

Fig. 2 shows a schematic setup of a second embodiment according to the present invention; and

Fig. 3 shows a schematic setup of third embodiment according to the present invention.

10

Fig. 1 shows a schematic overview 1 of a plant/process according to the present application. A conversion effluent 2 is fed to a first separator 3 wherein the conversion effluent is separated into three streams: process condensate 4, first product stream (liquid hydrocarbon stream) 5 and a gas stream 6.

The first product stream is fed to a second separator 7 wherein the first product stream is separated into a second product stream (product phase) 8 and a LPG stream comprising C3 - C4 wherefrom the recycle stream 9a is taken.

As described herein the first product stream is near H₂ free and H₂ is present predominantly in the gas phase in the first separator. Thus when the first product stream is separated into the second product stream 8 and the recycle stream the recycle stream obtained is a H₂ depleted recycle.

The second product stream 8 may be send to further processing, upgrade, storage etc.

The separation steps here illustrated by a single separator 7 may be carried in out in one or more separation steps in one or more separators. From the one or more separation steps may be separated one or more lower- and/or higher-
5 boiling phases. For example in addition to the two steams 9 and 8 shown, may be obtained a light fraction comprising e.g. CH₄, CO and/CO₂ together with H₂ if the first product stream 5 contains H₂ (not shown).

10 Fig. 2 shows a schematic overview 10 of a plant/process according to the present application. A conversion effluent 2 is fed to a first separator 3 wherein the conversion effluent is separated into three streams: process condensate 4, first product stream 5 and a gas stream 6. At least part of
15 the gas stream 6 is taken through a H₂ depletion step 11 whereby a H₂ depleted recycle stream 9b obtained.

The H₂ depletion step 11 may comprise e.g. a H₂ permeable membrane and/or a catalytic oxidation step.

20

Fig. 3 shows a schematic overview 12 of a plant/process wherein the embodiments of fig. 1 and 2 are combined where-
by a H₂ depleted stream is obtained from the gas stream 9b and from the LPG fraction taken from the second separator
25 as H₂ depleted stream 9a.

In the embodiments of fig. 1, 2 and 3 the one or more H₂ depleted streams are returned to the conversion step (not shown) from which the conversion effluent 2 is obtained.

30 The conversion step may be a MTG or a MTA process.

CLAIMS:

1. A process for production of hydrocarbons, comprising the steps of:

converting a feed stream comprising alcohols, ethers or mixtures hereof over a metal-containing zeolite based catalyst, active in dehydrogenation of hydrocarbons, in a conversion step thereby obtaining a conversion effluent including hydrogen,

separating said effluent to obtain an aqueous process condensate stream, a liquid hydrocarbon stream and a gaseous stream,

removing part of the hydrogen formed in the conversion step,

obtaining an at least partly H₂ depleted recycle stream, and

recycling at least part of the at least partly H₂ depleted recycle stream, the gaseous and/or liquid hydrocarbon streams to the conversion step, wherein:

the at least partly H₂ depleted recycle stream is obtained from the gaseous stream by passing said gaseous stream, after admixture with a predetermined amount of dioxygen, to a catalytic oxidation step, where hydrogen is reacted with said predetermined amount of dioxygen to form water and recycling said reacted stream, at least partly depleted in hydrogen, to the conversion step, and/or

the at least partly H₂ depleted recycle stream is obtained from the gaseous stream by passing said gaseous stream, after admixture with a predetermined amount of a

non-dioxygen hydrogen scavenger, to a catalytic oxidation step where hydrogen is reacted with said predetermined amount of the non-dioxygen hydrogen scavenger and recycling said reacted stream, at least partly depleted in hydrogen, to the conversion step.

2. The process according to claim 1 wherein hydrogen is removed by purging at least part of the gaseous recycle stream.

3. The process according to claim 1, wherein the at least partly H₂ depleted recycle stream is obtained from the gaseous stream by passing the gaseous stream to a hydrogen permselective membrane.

4. The process according to claim 1, wherein the liquid hydrocarbon stream is separated into a product phase and one or more lower- and/or higher-boiling phases, the at least one of the lower- and/or higher-boiling phases is at least partially recycled to the conversion step as the at least partly H₂ depleted recycle stream.

5. The process according to claim 1, wherein at least part of the gaseous stream is recycled to the conversion step.

6. The process according to claim 1, wherein the conversion step takes place in two or more consecutive reactors with quench addition of feed and recycle streams.

7. The process according to claim 3, wherein the permeation of H₂ in the selective membrane is adjusted to leave 1-10 mole % of H₂ in the retentate, recycled to the conversion step as the at least partly H₂ depleted recycle stream.

8. The process according to claim 1, wherein the hydrogen scavenger is an aldehyde, wherein said aldehyde and hydrogen is converted into an alcohol over a hydrogenation catalyst.

9. The process according to claim 1, wherein the hydrogen scavenger is formaldehyde and wherein formaldehyde and hydrogen is converted into methanol over a hydrogenation catalyst.

10. The process according to claim 1, wherein the hydrogen scavenger is hydrogen peroxide and wherein hydrogen peroxide and hydrogen is converted into water over a hydrogenation catalyst.

11. The process according to claim 1, wherein the at least part of the partly H₂ recycle stream or recycle streams is returned to one or more points upstream the conversion step.

12. The process according to claim 1, comprising a step regulating the H₂ content in the at least partly H₂ depleted recycle stream.

13. The process according to claim 1, wherein the zeolite based catalyst is a single bifunctional catalyst catalysing both methanol to hydrocarbons and dehydrogenation.
14. The process according to claim 1, wherein the zeolite based catalyst comprises a mixture of two or more catalysts which in combination catalyse both methanol to hydrocarbons and dehydrogenation reactions.
15. The process according to claim 1, wherein the zeolite based catalyst comprises a metal and/or metal oxide and a zeolite.
16. The process according to claim 1, wherein the zeolite based catalyst comprises a zeolite and a metal selected from the group consisting of Zn, Ga, In, Mo, Ag, P, Ge, Sn, Pd and Pt.
17. The process according to claim 16, wherein the metal is Zn.
18. The process according to claim 1, wherein the feed stream comprises methanol, dimethyl ether or mixtures hereof.
19. The process according to claim 1, wherein the process is carried out in one or more fixed bed reactors.

20. The process according to claim 1, wherein the process is carried out in one or more fluid bed reactors.

21. The process according to claim 1, wherein the dehydrogenation catalyst is arranged as a top layer in a conversion reactor and/or in one or more separate dehydrogenation reactors.

22. The process according to claim 1, wherein the hydrogen scavenger is carbon monoxide and/or carbon dioxide which are hydrogenated over a methanation catalyst.

23. A plant for the conversion of methanol to hydrocarbons comprising aromatics, said plant comprising:

means for supplying a feed stream comprising methanol, dimethyl ether or mixtures hereof

a conversion reactor,

a separator for separating a conversion effluent into a gaseous recycle stream, process condensate and a liquid product, and

means for removing H₂ from at least part of the effluent thereby obtaining at least one at least partly H₂ depleted recycle stream, wherein:

the means for removing H₂ from at least part of the effluent obtaining at least one at least partly H₂ depleted recycle stream is a selective oxidation step and/or a step, wherein a hydrogen scavenger is converted into methanol or water in the presence of H₂ and a hydrogenation catalyst.

24. The plant according to claim 23, wherein the means for removing H₂ from at least part of the effluent further comprises a selective membrane.

25. The plant according to claim 23, wherein the means for removing H₂ from at least part of the effluent further comprises: (i) means for separating a liquid hydrocarbon stream into at least a product phase and one or more lower- and/or higher-boiling phases and (ii) means for recycling at least one of said lower- and/or higher-boiling phases as the at least partly H₂ depleted recycle stream.

26. A plant for the conversion of methanol to hydrocarbons comprising aromatics according to the process of any one of claims 1 to 22.

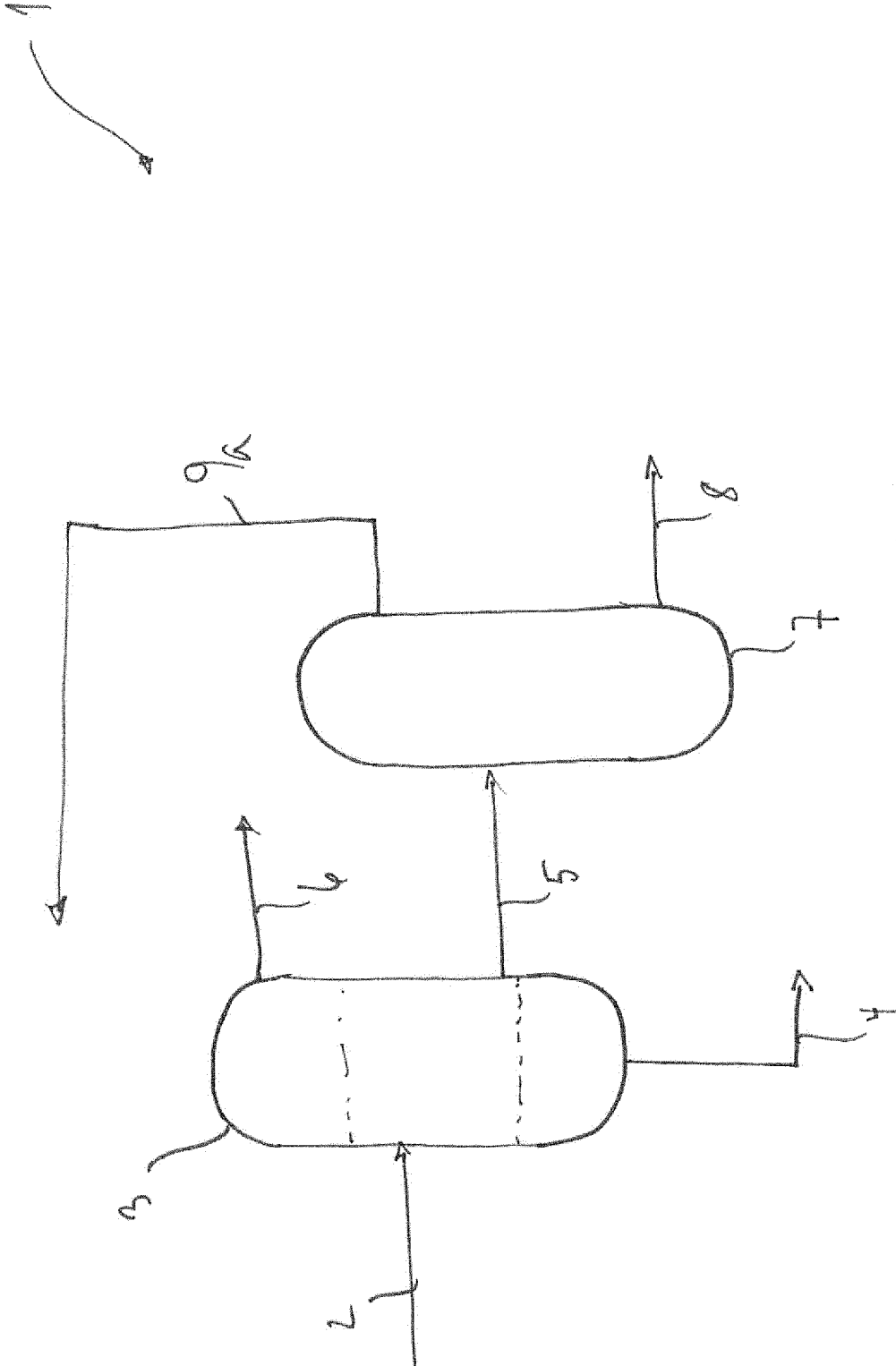


Fig 1

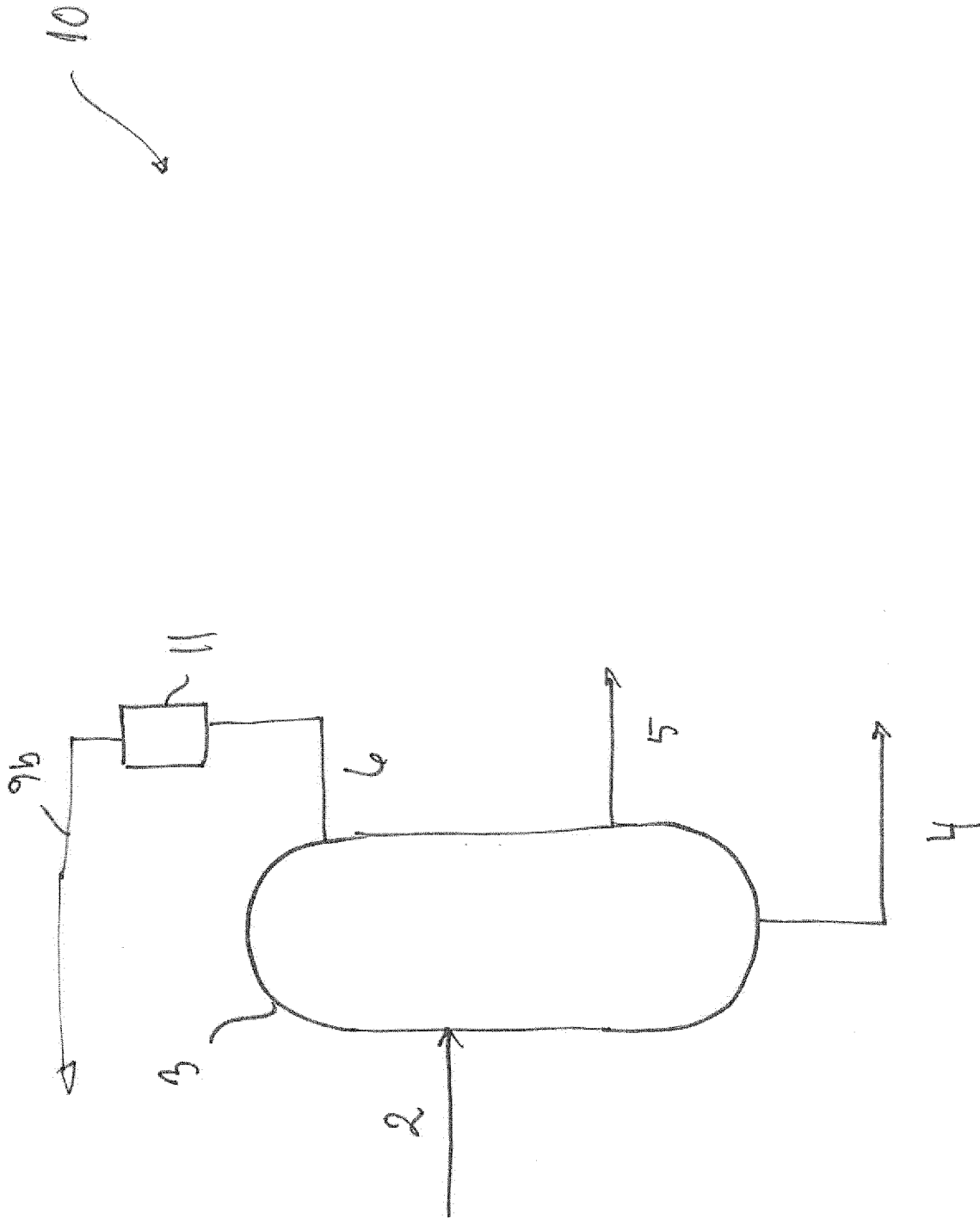


Fig. 2

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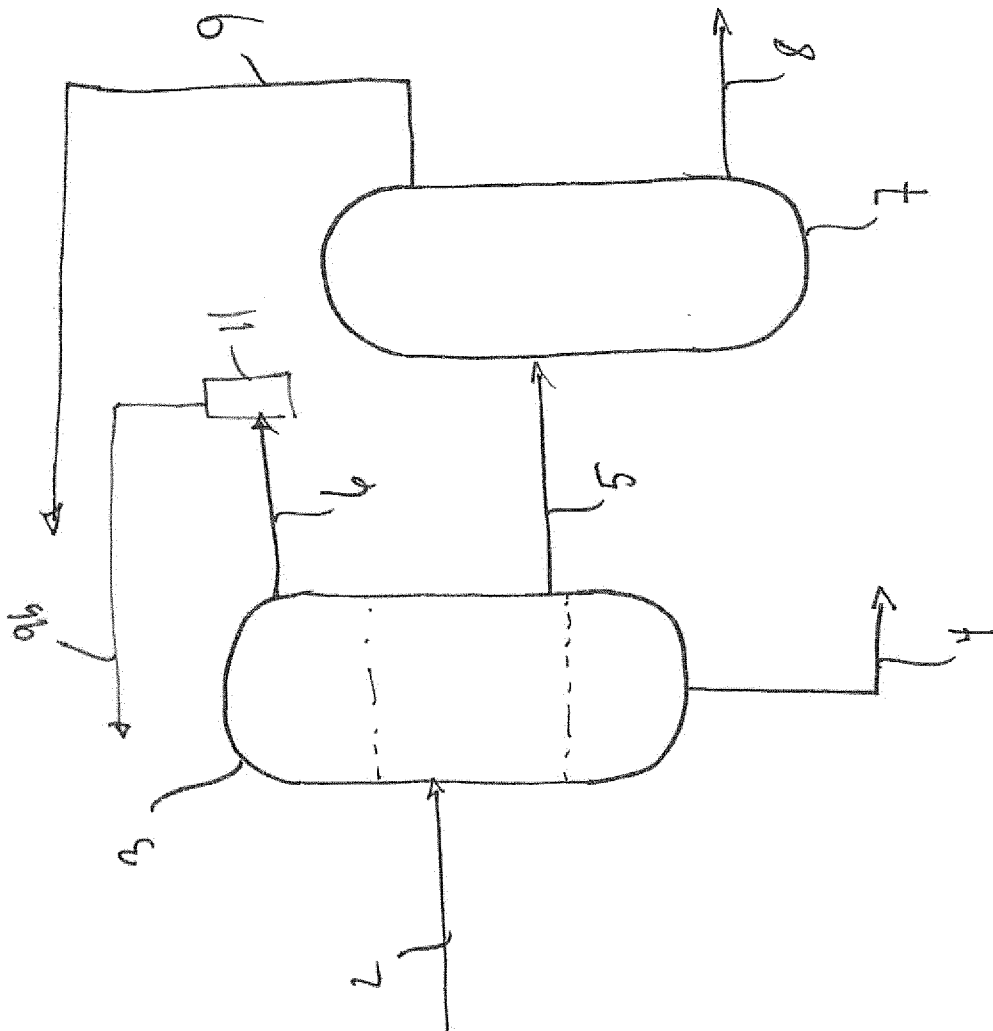


Fig 3