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(71) Applicant(s)
Shell Internationale Research Maatschappij B.V.

(72) Inventor(s)
Winter, Ferry;Chewter, Leslie Andrew;Van Westrenen, Jeroen

(74) Agent / Attorney
Pizzeys Patent and Trade Mark Attorneys, Level 14, ANZ Centre 324 Queen Street, Brisbane, QLD, 4000

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(71) Applicant *(for all designated States except US)*: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **VAN WESTRENEN, Jeroen** [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). **CHEWTER, Leslie Andrew** [GB/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). **WINTER, Ferry** [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).

(74) Agent: Shell International B.V.; Intellectual Property Services, PO Box 384, NL-2501 CJ The Hague (NL).

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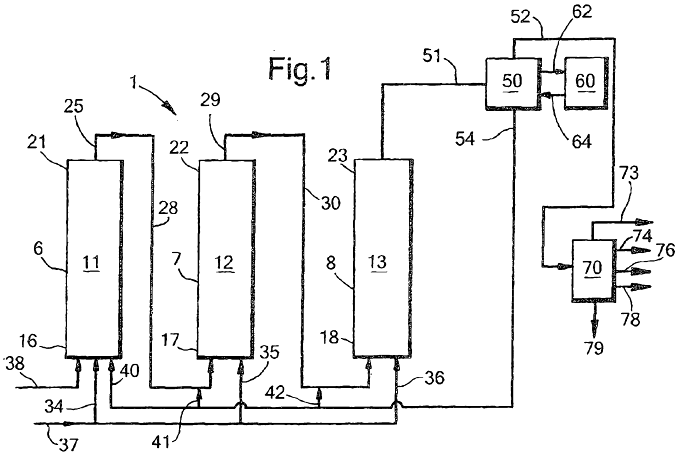

Fig.1

(57) Abstract: A process for converting an oxygenate to an olefin-containing product, wherein oxygenate is contacted with an oxygenate conversion catalyst in a reactor system comprising two or more serially arranged riser reactor stages to obtain a riser reactor effluent from each stage, wherein each riser reactor stage comprises a single riser reactor or a plurality of parallel riser reactors, such that at least part of the riser reactor effluent of a preceding riser reactor stage is fed into a subsequent riser reactor stage, and wherein oxygenate is added to a plurality of the riser reactor stages; and a reactor system comprising two or more serially arranged riser reactor stages wherein the first of the two or more serially arranged riser reactor stages has a smaller total cross-sectional area than at least one of the subsequent riser reactor stages.

WO 2009/065875 A1

PROCESS FOR CONVERTING AN OXYGENATE INTO AN OLEFIN-CONTAINING PRODUCT, AND REACTOR SYSTEM

This invention relates to a process for converting an oxygenate into an olefin-containing product, and to a reactor system suitable for such a process.

Processes for converting an oxygenate into an olefin-containing product are known in the art.

WO-A-01/62689 describes a process for converting oxygenate to an olefin-containing product comprising introducing oxygenate into a reactor system at plural stages along a flow axis of a reactor catalyst bed. For reactions of methanol over ZSM-34, SAPO-34, and of methanol with toluene over ZSM-5 catalysts, in a fluid-bed reactor it was shown, that ethylene selectivity improved when multiple feed injectors were used, however at a lower methanol conversion. It is pointed out that stagewise injection of reagents into several different and discrete zones has been used in various known fixed bed processes, but that these are disadvantageous for exothermic reactions with a negative impact on product selectivity.

As has been pointed out in WO 01/85872, WO 2004/31327 and WO 2004/37950, it can be beneficial to conduct an oxygenate-to-olefin conversion process in a hydrocarbon conversion apparatus containing a plurality of parallel-arranged riser reactors. Each individual riser reactor operates in a substantially identical manner, and in this way the conversion of the feed and selectivity to the desired products will be substantially identical in each riser reactor.

DE 100 27 159 discloses a methanol to propylene conversion process, wherein methanol is converted to a dimethylether containing vapour mixture using an Al_2O_3 catalyst, and wherein the dimethylether containing vapour mixture is contacted, together with additional water vapour, with a pentasil-type zeolite in at least two fixed-bed reactors, which allows to operate the reactors without indirect cooling.

US 2006/0135834 A1 discloses a process for converting oxygenate to olefin, wherein oxygenate is fed to a first stage of a reactor system having at least two stages, with cooling between the stages.

There is a need for an improved process for the conversion of oxygenate to olefin in a riser reactor system of industrial scale, wherein the selectivity of the process, such as in particular towards ethylene, can be optimised.

The present invention provides a process for converting an oxygenate to an olefin-containing product, wherein oxygenate is contacted with an oxygenate conversion catalyst in a reactor system comprising two or more serially arranged riser reactor stages to obtain a riser reactor effluent from each stage, wherein each riser reactor stage comprises a single riser reactor or a plurality of parallel riser reactors, such that at least part of the riser reactor effluent of a preceding riser reactor stage is fed into a subsequent riser reactor stage, and wherein oxygenate is added to a plurality of the riser reactor stages.

The invention is based on the insight gained by Applicant, that selectivity of an oxygenate conversion process towards desired olefins can be significantly improved using a serial riser reactor system, in which oxygenate feedstock is stagewise added to a plurality of the riser reactor stages, in particular to the first and at least one additional riser reactor stage. In addition to the improved selectivity, such as selectivity towards ethylene when converting methanol and/or dimethylether feedstock, the present invention provides further advantages in the economical implementation of the process, e.g. temperature control, catalyst deactivation, and solids handling, as will become clear hereinbelow.

In one embodiment, oxygenate is added to each of the riser reactor stages. Preferably the oxygenate is derived from a common oxygenate feedstock source. The common oxygenate feedstock source can for example be a storage vessel, feed line, or a pre-reactor. In this way oxygenate comprising feedstock of substantially the same composition is fed to and converted in each of the riser reactor stages. In one embodiment, the mass flow rate of oxygenate conversion catalyst in each subsequent riser reactor stage, after the first, to which oxygenate is added is higher than in the preceding riser reactor stage. Thus, the addition of fresh oxygenate feed is accommodated by additional oxygenate conversion catalyst. In this way the weight hourly space velocity (WHSV), defined as the throughput of the weight of reactants and reaction products per hour, and per weight of catalyst in the reactor, can be maintained above a selected minimum value, in order to achieve sufficient conversion.

Suitably, the total cross-sectional area of the last of the two or more serially arranged riser reactor stages is larger than the total cross-sectional area of the first of the riser reactor stages. The total cross-sectional area is the sum of the cross-sectional areas of all riser reactors in a particular stage. When there is only one riser reactor in a stage, its cross-section defines the total cross-sectional area. It is particularly beneficial if the total cross-sectional area of each subsequent riser reactor stage to which oxygenate is added, after the first, is higher than that of the preceding riser reactor stage. Increasing the cross-sectional area can partly or fully compensate for the increase in volumetric flow rate due to additional feedstock and catalyst, so that the flow velocity in the riser does not increase beyond critical values impeding for example conversion, catalyst stability and/or attrition.

The riser reactor effluent of a preceding reactor comprises gaseous effluent and solid oxygenate conversion catalyst. In one embodiment, at least 50 wt% of the gaseous effluent is fed to the subsequent riser reactor stage, in particular at least 80%, more in particular at least 90%. Further, it can be beneficial not to separate solids and gases between subsequent riser reactor stages. So, in a particular embodiment also at least 50 wt% of the solid oxygenate conversion catalyst is fed to the subsequent riser reactor stage, in particular at least 80%, more in particular at least 90%. More in particular, substantially all riser reactor effluent can be fed to the subsequent riser reactor stage.

The present invention has particular advantages in a process, wherein an olefinic feedstock is added to the first riser reactor stage. This olefinic co-feed allows conversion of the oxygenate by subsequent alkylation and cracking reactions. Staged addition of the oxygenate prevents alkylation to proceed too far in the first riser reactor stage, which would cause larger alkylates to form that would also lead to heavier cracking products. In particular ethylene selectivity is improved in this way.

The olefinic feedstock can with advantage be at least partially obtained from one of the riser reactor effluents, such as from the last riser effluent. This is possible during normal operation when oxygenates are converted to an olefin-containing product, and during start-up olefins from an external source may be used.

In one embodiment the oxygenate conversion catalyst comprises a molecular sieve having one-dimensional 10-membered ring channels, in particular a zeolite of the TON and/or MTT type, e.g. ZSM-22 and/or ZSM-23. These zeolite types have proven particularly effective for converting alcohols and ethers, such as methanol and/or dimethylether, and together with an olefinic co-feed such as butylenes, to ethylene and propylene with high selectivity for ethylene.

In one embodiment the oxygenate is contacted with the oxygenate conversion catalyst at a reaction temperature of more than 450°C, preferably at a temperature of 460°C or higher, more preferably at a temperature of 480°C or higher, even more preferably at a temperature of 490°C or higher.

In one embodiment the oxygenate added can be used for temperature control, and to this end the temperature of the oxygenate added to at least one of the riser reactors of any one of the riser reactor stages is set in dependence of a predetermined desired temperature in this riser reactor. For example, depending on the temperature and mass flow rate of the effluent stream from the previous riser reactor, the temperature and mass flow rate of additional catalyst, the temperature of the oxygenate can be set, e.g. by heat exchange, so that near the inlet of the riser reactor a predetermined inlet temperature of the mixture of the various feeds is realized.

In one embodiment, each gaseous effluent from one of the riser reactors has an oxygenate concentration below 10 wt%, in particular below 5 wt%, preferably below 2 wt%, more preferably below 1 wt%, still more preferably below 0.1 wt%. In this way, substantially full conversion of oxygenate in each riser reactor is realized. This is particularly beneficial at the last reactor effluent, as otherwise unreacted oxygenate has to be separated from the effluent in a work-up section. Separating e.g. unreacted methanol from water formed in the process is an undesirable and costly step in an industrial process.

In one embodiment, each gaseous effluent from one of the riser reactor stages, or preferably from all riser reactors individually, has a concentration of C5+ olefins (pentenes and higher olefins) of below 10 wt%, preferably below 5 wt%, more preferably below 2 wt%, yet more preferably below 1 wt%, still more preferably below 0.1 wt%. In particular, the C5+ olefins can comprise at least 50 wt% pentenes, more in particular at least 80 wt%, even more in particular at least 90 wt% of pentenes. In particular the pentene concentration of the gaseous effluent can be below 10 wt%, preferably below 5 wt%, more preferably below 2 wt%, yet more preferably below 1 wt%, still more preferably below 0.1 wt%.

In this way the ratio of C5+ olefins (in particular C5 olefins) to oxygenate at the subsequent riser inlet to which oxygenate is added is kept minimum in the process. Without wishing to be bound to a particular hypothesis, it is currently believed that keeping the ratio C5+ olefins/oxygenate, in particular C5 olefins/oxygenate, small is beneficial to ethylene selectivity, more in particular in the case that the oxygenate comprises oxygen-bonded methyl groups. It is currently believed that pentenes should be preferentially cracked to yield ethylene and propylene, as opposed to alkylation to higher olefins by reaction with the oxygenate. Cracking of higher olefins is thought to result is a lower concentration of ethylene in the final product.

The present invention also provides a reactor system comprising two or more serially arranged riser reactor stages including a first and at least one subsequent riser reactor stage, wherein each riser reactor stage comprises a single riser reactor or a plurality of parallel riser reactors and has a total cross-sectional area, wherein an inlet of a selected riser reactor of a subsequent stage is in fluid communication with an outlet of a riser reactor of a preceding stage, and wherein the first of the two or more serially arranged riser reactor stages has a smaller total cross-sectional area than at least one of the subsequent riser reactor stages.

Between 2 and 10, preferably between 2 and 5, more preferably three or four, riser reactor stages can be provided. Each riser reactor stage can comprise a single riser reactor. In one embodiment at least the last riser reactor stage comprises a plurality of parallel riser reactors.

An advantage of a riser stage comprising a plurality of parallel riser reactors is that the diameters of the individual riser reactors can be kept below a certain limit determined by engineering considerations, such as below 4 m, preferably below 3 m, or below 2.5 m, while a large total cross-sectional area of the riser reactor stage, defined as the sum of individual riser cross-sectional areas, can be arranged.

The invention will be described hereinbelow in more detail and by way of example with reference to the drawings, wherein

Figure 1 schematically shows a first embodiment of a serial riser reactor system for use in the present invention;

Figure 2 schematically shows a second embodiment of a serial riser reactor system for use in the present invention;

Figure 3 schematically shows a third embodiment of a serial riser reactor system for use in the present invention;

Figure 4 schematically shows the reaction network underlying model calculations;

Figure 5 schematically shows a first reactor system used in the model calculations; and

Figure 6 schematically shows a second reactor system used in the model calculations.

The present invention provides an improved process for converting an oxygenate to an olefin-containing product.

The olefin-containing product advantageously is a product containing lower olefins, in particular containing ethylene and/or propylene, more in particular the olefin-containing product contains at least 50 mol%, in particular at least 50 wt%, lower olefins (ethylene and propylene), based on total hydrocarbon product from the reaction. When a recycle of part of the product is used, the recycle stream is preferably not counted as olefin-containing product from the process. In a preferred embodiment the invention relates to a process for converting an oxygenate into an olefin-containing product with increased ethylene selectivity, i.e. with an increased ethylene/propylene ratio in the reaction product, in particular with a molar ethylene/propylene ratio of at least 0.5, such as of from 0.5 to 1.5.

Examples of an oxygenate that can be used as feedstock in the present invention include alcohols, such as methanol, ethanol, isopropanol, ethylene glycol, propylene glycol; ketones, such as acetone and methylethylketone; aldehydes, such as formaldehyde, acetaldehyde and propionaldehyde; ethers, such as dimethylether, diethylether, methylethylether, tetrahydrofuran and dioxane; epoxides such as ethylene oxide and propylene oxide; and acids, such as acetic acid, propionic acid, formic acid and butyric acid. Further examples are dialkyl carbonates such as dimethyl carbonate or alkyl esters of carboxylic acids such as methyl formate. Of these examples, alcohols and ethers are preferred.

Examples of preferred oxygenates include alcohols, such as methanol, ethanol, isopropanol, ethylene glycol, propylene glycol; and dialkyl ethers, such as dimethylether, diethylether, methylethylether. Cyclic ethers such as tetrahydrofuran and dioxane, are also suitable.

The oxygenate used in the process according to the invention is preferably an oxygenate which comprises at least one oxygen-bonded alkyl group. The alkyl group preferably is a C1-C4 alkyl group, i.e. comprises 1 to 4 carbon atoms; more preferably the alkyl group comprises 1 or 2 carbon atoms and most preferably one carbon atom. The oxygenate can comprise one or more of such oxygen-bonded C1-C4 alkyl groups. Preferably, the oxygenate comprises one or two oxygen-bonded C1-C4 alkyl groups.

More preferably an oxygenate is used having at least one C1 or C2 alkyl group, still more preferably at least one C1 alkyl group.

Preferably the oxygenate is chosen from the group of alkanols and dialkyl ethers consisting of dimethylether, diethylether, methylethylether, methanol, ethanol and isopropanol, and mixtures thereof.

Most preferably the oxygenate is methanol or dimethylether.

In one embodiment, the oxygenate is obtained as a reaction product of synthesis gas. Synthesis gas can for example be generated from fossil fuels, such as from natural gas or oil, or from the gasification of coal. Suitable processes for this purpose are for example discussed in Industrial Organic Chemistry, Klaus Weissermehl and Hans-Jürgen Arpe, 3rd edition, Wiley, 1997, pages 13-28. This book also describes the manufacture of methanol from synthesis gas on pages 28-30.

In another embodiment the oxygenate is obtained from biomaterials, such as through fermentation. For example by a process as described in DE-A-10043644.

By an olefin-containing product is understood a product consisting of or comprising an olefin. By an olefin is understood an organic compound containing at least two carbon atoms connected by a double bond. The product can comprise a mixture of different olefins. The product can be a mixture further comprising other one or more other hydrocarbonaceous and non-hydrocarbonaceous components, such as saturates, aromatic compounds, oxygenates, water, carbon monoxide, carbon dioxide.

In the present invention, oxygenate is contacted with an oxygenate conversion catalyst.

By an oxygenate conversion catalyst is understood a catalyst that is able to convert oxygenate into olefin. Any catalyst known to be able to convert oxygenate into olefin under suitable conditions may be used. Examples include catalysts comprising a molecular sieve, for example silico-alumino phosphates such as SAPO-34 (CHA type), and zeolite catalysts such as ZSM-22, ZSM-23, and ZSM-5.

The expression ‘molecular sieve’ is used in the description and claims for a material containing small regular pores and/or channels and exhibiting catalytic activity in the conversion of oxygenate to olefin. The molecular sieve can in particular be a zeolite. A zeolite is understood to be an aluminosilicate molecular sieve. Where reference is made in the description and in the claims to a molecular sieve, this can in particular be a zeolite.

Molecular sieve and zeolite types are for example defined in Ch. Baerlocher and L.B. McCusker, Database of Zeolite Structures: http://www.iza-structure.org/databases/, which database was designed and implemented on behalf of the Structure Commission of the International Zeolite Association (IZA-SC), and based on the data of the 4th edition of the Atlas of Zeolite Structure Types (W.M. Meier, D.H. Olson and Ch. Baerlocher).

The oxygenate conversion catalyst can be a zeolite catalyst. By a zeolite catalyst is understood a catalyst consisting of or containing a zeolite. Reference herein to zeolite is to a pure zeolite or to the zeolite portion of a catalyst containing other components as well.

Preferably, at least part of the molecular sieve is a molecular sieve comprising a 10-membered ring channel. More preferably this molecular sieve is a molecular sieve having one-dimensional 10-membered ring channels. A molecular sieve having one-dimensional 10-membered ring channels is understood to be a molecular sieve having only 10-membered ring channels in one direction which are not intersected by other 8, 10 or 12-membered ring channels from another direction.

Preferably, the oxygenation catalyst comprises a molecular sieve selected from the group of TON-type (for example zeolite ZSM-22), MTT-type (for example zeolite ZSM-23), STF-type (for example SSZ-35), SFF-type (for example SSZ-44), EUO-type (for example ZSM-50), and EU-2-type molecular sieves or mixtures thereof.

MTT-type catalysts are more particularly described in e.g. US-A-4,076,842. For purposes of the present invention, MTT is considered to include its isotypes, e.g., ZSM-23, EU-13, ISI-4 and KZ-1.

TON-type molecular sieves are more particularly described in e.g. US-A-4,556,477. For purposes of the present invention, TON is considered to include its isotypes, e.g., ZSM-22, Theta-1, ISI-1, KZ-2 and NU-10.

EU-2-type molecular sieves are more particularly described in e.g. US-A-4,397,827. For purposes of the present invention, EU-2 is considered to include its isotypes, e.g., ZSM-48.

In a further preferred embodiment a molecular sieve of the MTT-type, such as ZSM-23, and/or a TON-type, such as ZSM-22 is used.

The preferred zeolites used in the present invention are distinct from zeolites having small pore 8-ring channels or zeolites having large pore 12-ring channels.

In one embodiment, molecular sieves (zeolites) in the hydrogen form are used, e.g., HZSM-22, HZSM-23, HZSM-48, HZSM-5. Preferably at least 50% w/w, more preferably at least 90% w/w, still more preferably at least 95% w/w and most preferably 100% of the total amount of molecular sieve used is in the hydrogen form, based on total molecular sieve in the oxygenate conversion catalyst. When the molecular sieves are prepared in the presence of organic cations the molecular sieve may be activated by heating in an inert or oxidative atmosphere to remove organic cations, for example, by heating at a temperature over 500 °C for 1 hour or more. The zeolite is typically obtained in the sodium or potassium form. The hydrogen form can then be obtained by an ion exchange procedure with ammonium salts followed by another heat treatment, for example in an inert or oxidative atmosphere at a temperature over 500 °C for 1 hour or more. The molecular sieves obtained after ion-exchange are also referred to as being in the ammonium form. Preferably the zeolite has a silica to alumina ratio (SAR) in the range from 1 to 1000. The SAR is defined as the molar ratio of SiO_2/Al_2O_3 corresponding to the composition of the molecular sieve.

For ZSM-22, a SAR in the range of 40-150 is preferred, in particular in the range of 70-120. Good performance in terms of activity and selectivity has been observed with a SAR of about 100.

For ZSM-23, a SAR in the range of 20-120 is preferred, in particular in the range of 30-80. Good performance in terms of activity and selectivity has been observed with a SAR of about 50.

For ZSM-5, a SAR of 60 or higher is preferred, in particular 80 or higher, more preferably 100 or higher, still more preferably 150 or higher, such as 200 or higher.

The molecular sieve can be used as such or in a formulation, such as in a mixture or combination with a so-called binder material, e.g. silicabinder, aluminabinder, silica-alumina binder, zirconiabinder, and/or a filler material, e.g. kaolin, kaolinit, attapulgite, montmorillonite, bentonite, alumina, silica, titania, and optionally also with an active matrix component. Other components can also be present in the formulation. Typically, molecular sieve content, such as in particular zeolite content, in a formulated catalyst is in the range of from 1 wt% to 50 wt%, preferably 10 to 40 wt%, more preferably 20 to 40 wt%, based on total formulated catalyst.

If one or more molecular sieves are used as such, in particular when no binder, filler, or active matrix material is used, the molecular sieve(s) itself is/are referred to as oxygenate conversion catalyst. In a formulation, the molecular sieve(s) in combination with the other components of the mixture such as binder and/or filler material is/are referred to as oxygenate conversion catalyst.

It is desirable to provide a oxygenate conversion catalyst having good mechanical or crush strength, because in an industrial environment the catalyst is often subjected to rough handling which tends to break down the catalyst into powder-like material. The latter causes problems in the processing, such as attrition of catalyst particles in a riser reactor. Preferably the molecular sieve is therefore incorporated in a binder material. Examples of suitable materials in a formulation include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica, alumina, aluminosilicate. For present purposes, inactive materials of a low acidity, such as silica, are preferred because they may prevent unwanted side reactions which may take place in case a more acidic material, such as alumina is used.

According to the present invention, oxygenate is contacted with the oxygenate conversion catalyst in two or more serially arranged riser reactors such that at least part of the riser reactor effluent of a preceding riser reactor is fed into a subsequent riser reactor, and wherein oxygenate is added to a plurality of the riser reactors.

By a riser reactor is understood an upright, such as essentially vertical, reactor where a feed or feed mixture can be added at the lower end of the reactor, together with a catalyst, and an effluent comprising reaction product and catalyst can be obtained at the top of the reactor. The catalyst is typically fluidised, and the flow velocity in the riser is higher than the minimum fluidization velocity of the catalyst particles.

In the process of the invention two or more serially arranged riser reactors are used. By serially arranged is understood that at least part of the riser reactor effluent of a preceding riser reactor is fed into a subsequent riser reactor, which subsequent riser reactor is connected directly or indirectly with the first riser reactor via one or more conduits.

US patent specification No. 6 791 002 B1 discloses a riser reactor system for conversion of hydrocarbon feedstock, in particular naphtha, to ethylene and propylene. Particular embodiments include a plurality of riser reactor units placed in a series configuration. The use of a series of reactor units provides for addition of fresh catalyst to separate individual reactor units, and also permits control of feeding different hydrocarbon feedstocks, to the individual separate riser reactors, so as to control the reaction time and reaction conditions for different feedstocks. Different hydrocarbon feedstocks that are cracked in the individual riser reactors can be different recycle streams that are obtained from fractionation of the gas coming off the final riser reactor. US ‘002 relates to conventional cracking of naphtha feedstock, and not to the conversion of oxygenate.

Preferably, in the present invention 2 to 10 serially arranged riser reactors are used, more preferably 2 to 5 riser reactors. Most preferably 3 or 4 serially arranged riser reactors are used, as these can provide the best compromise between maximising selectivity and minimizing complexity and cost.

The height of the riser reactors used in the process of the invention may vary widely. For practical purposes, however, suitable heights lie in the range from 2 to 100 meters. Preferably the riser reactors used in the process of the invention have a height in the range from 5 to 70 meters, more preferably in the range from 10 to 60 meters.

The diameter of the riser reactors used in the process of the invention may vary widely. For practical purposes, however, suitable diameters lie in the range from 0.01 to 10 meters. Preferably the riser reactors used in the process of the invention have a diameter in the range from 0.05 to 5 meters, more preferably in the range from 0.1 to 3 meters.

In a preferred embodiment the reactor diameter, and thereby the cross sectional area, of each subsequent riser reactor is greater than the preceding riser reactor. Suitably each subsequent riser reactor has a diameter in the range from 1-200%, preferably in the range from 10-100%, more preferably in the range from 20-70% greater than the diameter of the preceding riser reactor. For example if 3 riser reactors are used, the first riser reactor may have a diameter in the range from 0.5 to 2 meter; the second riser reactor may have a diameter in the range from 0.55 to 4 meter and the third riser reactor may have a diameter in the range from 0.6 to 6 meter.

Oxygenate may be provided as an oxygenate comprising feedstock of substantially the same composition to each of the respective riser reactors. In particular, the oxygenate can be derived from a common oxygenate feedstock source such as feed line or upstream process unit, e.g. a pre-reactor. A suitable prereactor converts alkylalcohol, in particular methanol, at least partially into dialkylether, in particular dimethylether. Water is also formed, and preferably separated from the oxygenate feed to the oxygenate conversion process, preferably such that the oxygenate feed contains dimethylether, optionally methanol, and at most 5%wt of water. In this way, less water is formed in the process of converting oxygenate to olefins, which has advantages for the process design and lowers hydrothermal deactivation of catalysts. The oxygenate comprising feedstock can be divided by a distributor to each of the riser reactors or multiple supplies to the riser reactors may be arranged. The oxygenate may be mixed with another stream such as with effluent from a preceding riser reactor before entering a subsequent riser reactor, or the oxygenate may be added to a subsequent riser reactor separately from the effluent of a preceding riser reactor. Preferably the oxygenate is mixed with effluent of a preceding riser reactor before entering a subsequent riser reactor. By mixing such oxygenate with product effluent from a preceding riser reactor, the temperature of the feed mixture of oxygenate and product effluent into a subsequent riser reactor may be controlled.

The present invention has particular advantages in a process, wherein an olefinic feedstock is added to the first riser reactor together with the oxygenate. An alcohol or ether oxygenate can be converted to an olefinic product by an initial alkylation step with an olefin from the olefinic co-feed, followed by cracking. If high ethylene selectivity is desired, and the oxygenate comprises oxygen-bonded methyl groups such as in methanol or dimethylether, an optimum reaction pathway is achieved with a butene co-feed, which is alkylated to a pentene and subsequently cracked into one ethylene and one propylene. The cracking reaction should take place faster than the further alkylation of the pentene to a hexene. Therefore it is beneficial if the oxygenate is fed stagewise, otherwise the initial concentration of oxygenate is so high that the alkylation reaction proceeds too far initially. It can be preferred that the amount of oxygenate added to each of the subsequent riser stages is substantially equal, such as within 20% from an average feed rate of oxygenate to the riser stages, preferably within 10%.

It is further preferred for optimum ethylene selectivity to keep the C5+ olefin concentration, in particular the C5 olefin concentration, minimum at the inlet of each riser reactor to which oxygenate is added. Cracking of longer olefins but pentene is thought to result in a lower portion of ethylene being formed.

It has been found that particularly useful oxygenation catalysts for carrying out both the alkylation and cracking reactions comprises a molecular sieve having one-dimensional 10-membered ring channels, such as of the TON or MTT type, e.g. zeolite ZSM-22 and/or ZSM-23, based on the total amount of molecular sieve in the catalyst.

In one embodiment the oxygenate conversion catalyst can comprise more than 50 wt%, based on total molecular sieve in the oxygenate conversion catalyst, of one-dimensional molecular sieve having 10-membered ring channels, and in a further embodiment at least 65 wt%. The presence of a large majority of such molecular sieve strongly determines the predominant reaction pathway.

In a special embodiment the oxygenate conversion catalyst comprises, in addition to molecular sieve having one-dimensional 10-membered ring channels, at least 1 wt%, based on total molecular sieve in the oxygenate conversion catalyst, of a further molecular sieve having more-dimensional channels, in particular at least 5 wt%, more in particular at least 8 wt%. The presence of a minority portion of a more-dimensional molecular sieve in the oxygenate conversion catalyst was found to improve stability (slower deactivation during extended runs) and hydrothermal stability. Without wishing to be bound by a particular hypothesis or theory, it is presently believed that this is due to the possibility for converting larger molecules by the more-dimensional molecular sieve, that were produced by the 1-dimensional molecular sieve, and which would otherwise form coke. The further molecular sieve can for example be a MFI-type molecular sieve such as ZSM-5, or a SAPO-type molecular sieve such as SAPO-34. The weight ratio between the molecular sieve having one-dimensional 10-membered ring channels, and the further molecular sieve having more-dimensional channels can be in the range of from 1:1 to 100:1.

Preferably the further molecular sieve is a MFI-type molecular sieve, in particular zeolite ZSM-5, having a Silica-to-Alumina ratio SAR of at least 60, more preferably at least 80, even more preferably at least 100, yet more preferably at least 150. At higher SAR the percentage of C4 saturates in the C4 totals produced is minimized. In special embodiments the oxygenate conversion catalyst can comprise less than 35 wt% of the further molecular sieve, based on the total molecular sieve in the oxygenate conversion catalyst, in particular less than 20 wt%, more in particular less than 18 wt%, still more in particular less than 15 wt%.

Preferably the oxygenate is fed to the first riser reactor together with an olefinic co-feed. An additional olefinic co-feed can also be added to the effluent of a preceding riser reactor that is fed into a subsequent riser reactor (i.e. an additional olefinic co-feed can be added in between riser reactors). As, however, the effluent of the preceding riser reactor already contains olefins, any olefinic co-feed is preferably only added to the first riser reactor.

By an olefinic composition or stream, such as an olefinic product, product fraction, fraction, feedstock, co-feed, effluent or the like is understood such a composition or stream comprising one or more olefins, unless specifically indicated otherwise. Other species can be present as well. The olefinic composition or stream can comprise one olefin or a mixture of olefins. The expression olefin-containing product is used synonymously with olefinic product.

By an olefinic co-feed is understood a feed containing one or more olefins. The olefinic co-feed can contain one olefin or a mixture of olefins. The olefinic co-feed can contain a mixture of olefins. Apart from olefins, the olefinic co-feed may contain other hydrocarbon compounds, such as for example paraffinic, alkylaromatic, aromatic compounds or a mixture thereof. Preferably the olefinic co-feed comprises an olefinic portion of more than 50 wt%, more preferably more than 60 wt%, still more preferably more than 70 wt%, which olefinic fraction consists of olefin(s). The olefinic co-feed can also consist essentially of olefin(s).

Any non-olefinic compounds in the olefinic co-feed are preferably paraffinic compounds. If the olefinic co-feed contains any non-olefinic hydrocarbon, these are preferably paraffinic compounds. Such paraffinic compounds are preferably present in an amount in the range from 0 to 50 wt%, more preferably in the range from 0 to 40 wt%, still more preferably in the range from 0 to 30 wt%.

By an olefin is understood an organic compound containing at least two carbon atoms connected by a double bond. A wide range of olefins can be used. The olefin can be a mono-olefin, having one double bond, or a poly-olefin, having two or more double bonds. Preferably olefins present in the olefinic co-feed are mono-olefins.

The olefin(s) can be a linear, branched or cyclic olefin. Preferably olefins present in the olefinic co-feed are linear or branched olefins.

Preferred olefins have in the range from 2 to 12, preferably in the range from 3 to 10, and more preferably in the range from 4 to 8 carbon atoms.

Examples of suitable olefins that may be contained in the olefinic co-feed include ethene, propene, butene (one or more of 1-butene, 2-butene, and/or iso-butene (2-methyl-1-propene)), pentene (one or more of 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, and/or cyclopentene), hexene (one or more of 1-hexene, 2-hexene, 3-hexene, 2-methyl-1-pentene, 2-methyl-2-pentene, 3-methyl-1-pentene, 3-methyl-2-pentene, 4-methyl-1-pentene, 4-methyl-2-pentene, 2,3-dimethyl-1-butene, 2, 3-dimethyl-2-butene, 3,3-dimethyl-1-butene, methylcyclopentene and/or cyclohexene), heptenes, octenes, nonenes and decenes. The preference for specific olefins in the olefinic co-feed may depend on the purpose of the process. The olefinic feedstock can comprise propylene. Also light olefins propylene and even ethylene can be recycled from a reactor effluent, although recycling substantial amounts of ethylene is a less preferred option. In particularly preferred embodiments, ethylene is not recycled, and this is clearly so when a high ethylene yield is desired which is often the case. Recycling part or all of the propylene may be an interesting option for maximising ethylene selectivity of the overall process, but when it is desired to maximise ethylene+propylene yield, it is not preferred to recycle propylene.

In one embodiment the olefinic co-feed contains olefins having 4 or more carbon atoms (i.e. C_4+ olefins), such as butenes, pentenes, hexenes and heptenes. Preferably the olefinic portion of the olefinic co-feed comprises at least 50 wt% of butenes and/or pentenes, preferably at least 50 wt% of butenes. More preferably the olefinic fraction of the olefinic co-feed comprises at least 70 wt% of butenes and/or pentenes, most preferably at least 70 wt% of butenes. Butenes as co-feed have been found to be particularly beneficial for high ethylene selectivity.

The ethylene selectivity of the process can be increased when the olefinic co-feed comprises less than 10 wt% of C5+ olefins, in particular less than 10 wt% of C5+ olefins and paraffins, more in particular less than 10 wt% of C5+ hydrocarbon species. C5+ denotes hydrocarbons with 5 or more carbon atoms. It is also preferred that the feed to the reactor system, in particular an olefinic feedstock, comprises low amounts of aromatics, such as 10 wt% or less, preferably 5 wt% or less, more preferably 1 wt% or less, of C6-C8 aromatics, based on total hydrocarbons. When part of a reactor effluent is to be recycled, these preferred limits apply as well to the effluent. So, the reactor effluent from each of the riser reactors suitably comprises 10 wt% or less, preferably 5 wt% or less, more preferably 1 wt% or less, of C6-C8 aromatics, based on total hydrocarbons in the effluent.

Preferably reaction product containing one or more olefins is separated into one or more fractions, preferably at least a product fraction containing olefins intended as a product and a further fraction. Preferably at least part of the further fraction is recycled to the start of the process as (all or part of) the olefinic co-feed. The product fraction can be a lighter fraction than the recycle fraction, and there can also be one or more further fractions heavier than the recycle fraction. The product fraction can for example mainly comprise ethylene and propylene, the recycle fraction mainly butylenes, and the further fraction mainly C5+ olefins.

The olefinic co-feed preferably consists, during normal operation, for at least 50 wt%, more preferably at least 80 wt%, still more preferably from 90 to 100 wt% of such a recycle fraction of the reaction product. In a specifically preferred embodiment the olefinic co-feed consists essentially of a recycle fraction of the reaction product. If that is not the case, part of the olefinic co-feed can originate from an external source, in particular during start-up when no or insufficient olefinic reaction products are available. Preferably, at least 70 wt% of the olefinic feedstock in step a) of the process, during normal operation, is formed by a recycle stream obtained from fractionation of a riser reactor effluent, preferably at least 90 wt%, more preferably at least 99 wt%, and most preferably the olefinic feedstock is during normal operation formed by the recycle stream. In a preferred embodiment of a process with olefinic co-feed, the olefinic feedstock comprises at least 50 wt% of C4 olefins, and at least a total of 70 wt% of C4 hydrocarbon species. It is believed that this increases ethylene selectivity. The preferred molar ratio of oxygenate in the oxygenate feedstock to olefin in the olefinic co-feed depends on the specific oxygenate used and the number of reactive oxygen-bonded alkyl groups therein. Preferably the molar ratio of oxygenate to olefin in the total feed lies in the range of 10:1 to 1:10, more preferably in the range of 5:1 to 1:5 and still more preferably in the range of 3:1 to 1:3.

In a preferred embodiment wherein the oxygenate comprises only one oxygen-bonded methyl group, such as methanol, the molar ratio preferably lies in the range from 5:1 to 1:5 and more preferably in the range of 2.5:1 to 1:2.5.

In another preferred embodiment wherein the oxygenate comprises two oxygen-bonded methyl groups, such as for example dimethylether, the molar ratio preferably lies in the range from 5:2 to 1:10 and more preferably in the range of 2:1 to 1:4. Most preferably the molar ratio in such a case is in the range of 1.5:1 to 1:3.

In addition to the oxygenate, and the olefinic co-feed, a diluent may be fed into the first riser reactor and/or any subsequent riser reactor. It is preferred to operate without a diluent, or with a minimum amount of diluent, such as less than 200 wt% of diluent based on the total amount of oxygenate feed, in particular less than 100 wt%, more in particular less than 20 wt%. Any diluent known by the skilled person to be suitable for such purpose can be used. Such diluent can for example be a paraffinic compound or mixture of compounds. Preferably, however, the diluent is an inert gas. The diluent can be argon, nitrogen, and/or steam. Of these, steam is the most preferred diluent. For example, the oxygenate feed and optionally olefinic co-feed can be diluted with steam, for example in the range from 0.01 to 10 kg steam per kg oxygenate feed. Preferably the diluent, in particular steam, is less than 50 vol%, more preferably less than 30 vol%, of the total feedstock to the process, in particular less than 50 vol%, preferably less than 30 vol%, based on the total of oxygenate and diluent feed to the process.

The process can be carried out over a wide range of temperatures and pressures. Preferably, however, the hydrocarbon feed is contacted with the oxygenate conversion catalyst at a temperature in the range from

200 °C to 650 °C. In a further preferred embodiment the temperature is in the range from 250 °C to 600 °C, more preferably in the range from 300 °C to 550 °C, most preferably in the range from 450 °C to 550 °C. In one embodiment, the temperature in the different reactor stages is substantially the same, i.e. within 20 °C, more in particular within 5 °C from each other. Since typically there will be a temperature profile along the flow direction of the reactors, for this purpose the temperature can be the temperature at the inlet zone of a reactor stage, or alternatively the maximum temperature in a reactor stage, or alternatively an average temperature in a reactor stage.

In the presence of a molecular sieve having one-dimensional 10-membered ring channels the oxygenate conversion reaction is preferably conducted at a temperature of more than 450 °C, preferably at a temperature of 460 °C or higher, in particular 480 °C or higher, more preferably at a temperature of 490 °C or higher. At higher temperatures a higher activity and ethylene selectivity is observed. One-dimensional molecular sieves having 10-membered ring channels can be operated under oxygenate conversion conditions at such high temperatures with acceptable deactivation due to coking, contrary to molecular sieves with smaller pores or channels, such as 8-membered ring channels. Temperatures referred to hereinabove represent reaction temperatures, and it will be understood that a reaction temperature can be an average of temperatures of various feed streams and the catalyst in the reaction zone.

The pressure can vary widely, preferably a pressure in the range from 1 to 8 bar is applied, more preferably a pressure in the range of 1 to 5 bar is applied.

In the process according to the invention the feed to the riser reactors is preferably fed to such riser reactors in gaseous state. Preferably the feed is vaporized, if necessary, and subsequently mixed with the catalyst particles.

Figure 1 illustrates schematically an embodiment of a serial riser reactor system provided for carrying out the process according to the invention.

The reactor system 1 has three riser reactor stages 6,7,8 each having a single riser reactor 11,12,13, which riser reactors are serially arranged. Stage 6 with riser 11 is the first riser reactor stage, stage 7 with riser 12 is the second stage (riser), and stage 8 with riser 13 is the third stage (riser). Each riser has at its lower end an inlet end 16,17,18 with one or more inlets, and at its upper end an outlet end 21,22,23 with one or more outlets. The outlet 25 of the first riser 11 is connected via a conduit 28, such as a downer, to the inlet end 17 of the second riser 12. Likewise, outlet 29 of the second riser 12 is connected via a conduit 30 to the inlet end 18 of the third riser 13.

Each riser is moreover arranged to receive oxygenate at its inlet end, via conduits 34,35,36 which are all connected to oxygenate feedstock line 37. The first riser 11 has moreover an inlet for an olefinic co-feed from line 38, and an inlet for oxygenation catalyst via line 40. The feed lines 34,28 and 40 are shown to enter the inlet end 16 separately, but it will be understood that any two or all three feed lines can be combined before entering the inlet end 16.

To the effluent from riser 11, entering the inlet end 17 of the second riser 12 is added further oxygenation catalyst via line 41, wherein it will be understood that the catalyst can alternatively be added to the inlet end 17 directly. Likewise, oxygenation catalyst is added to the inlet end 18 of riser 13 via line 42.

The outlet from the last riser 13 is connected to a collector and vapour/solids separator unit 50 via line 51. The unit 50 can also be integrated with the outlet end of the last riser. It can be a large collector vessel combined with a plurality of cyclone separators, which can be internally housed in the collector vessel. The unit 50 has an outlet for vapour 52 and an outlet for catalyst 54, to which the catalyst feed lines 40,41,42 are connected. There is moreover provided a catalyst regeneration unit 60 which is arranged to receive catalyst via line 62 and returns regenerated catalyst to the unit 50 via line 64.

During normal operation of the reactor system 1, oxygenate, olefinic co-feed and oxygenation catalyst are fed via lines 34, 38, 40, respectively, to the inlet end 16 of the first riser 11. Conversion in the first riser 11 over the oxygenation catalyst forms an olefinic first reactor effluent comprising a gaseous product comprising olefins, and catalyst. Substantially the entire reactor effluent is fed in this example via line 28 to the inlet end 17 of the second riser 12, together with oxygenate from line 35 and additional catalyst via line 41. Although it is possible to also feed an olefinic co-feed to the second riser 12, this is not needed and not necessarily advantageous, since the effluent from reactor 11 already contains olefins.

Additional oxygenation catalyst is added via line 41. Thus, the mass flow rate (mass per unit of time) of oxygenate conversion catalyst in the second riser is higher than in the first riser reactor. As shown in the drawing, it is premixed with the reactor effluent in line 29, but can also directly be admitted to the inlet end 17. The cross-section of the second riser is larger than that of the first riser. A useful design rule is to choose the cross-section increase from one riser to the next such that the weight hourly space velocity remains substantially constant, i.e. not deviating more than 50% from that of the previous riser reactor. For cylindrical risers, the increase in cross-section can also be expressed as an increase in diameter.

The weight hourly space velocity is suitably chosen such that a desired conversion is achieved at the outlet of the reactor.

When the weight hourly space velocity is substantially constant, the time to flow through the riser is the same for risers of the same height (as they are shown in the example).

The conversion in the second riser 12 proceeds similar to that in the first riser 11, wherein the role of the olefinic co-feed is taken over by the olefinic product in the effluent from the first riser.

Effluent from the second riser 12 is fed to the inlet end 18 of the third riser 13, and combined with additional feeds of oxygenate via line 36 and oxygenation catalyst via line 42, in principle in the same way as discussed for the inlet end 17 of the second riser 12.

The cross section of the third riser 13 is again larger than that of the second riser. It can be preferred to design each riser and the respective catalyst throughput such that substantially full conversion of oxygenate is achieved in the riser, this can be most desirable for the last riser so that substantially no oxygenate forms part of the effluent from the last riser.

The effluent from the outlet end 23 of the last riser 13 comprises olefin-containing product and catalyst. The product is separated from the catalyst in the collection and vapour/solids separator unit 50.

Under typical operating conditions the deactivation of oxygenate catalyst, such as due to coking, occurs on a timescale much longer than the average contact time the riser reactors. In such circumstances it is not needed to regenerate all of the catalyst in the unit 50. It is rather sufficient then to only send a portion of the catalyst to the catalyst regeneration unit 60, where typically coke is burned partially or substantially fully at temperatures of about 600 °C or more. The size of the portion sent to the regeneration unit 60 depends on the average degree of deactivation or coking, and on the regeneration conditions, e.g. partial or full burning of coke. Coke concentration of the catalyst leaving the last reactor stage is preferably less than 10 wt% based on coked catalyst, more preferably less that 5 wt%, and therefore the performance of the catalyst through the various stages does not change substantially. In particular, when the catalyst includes molecular sieve having one-dimensional 10-membered ring channels, more in particular as the majority molecular sieve component, and preferably with an olefinic co-feed, the oxygenate conversion reaction does not require a particular coke level on the catalyst for good performance.

It will be understood that it is also possible to arrange more vapour/solids separators, such as one for each outlet from a riser reactor. In the latter case, effluent from each riser reactor is separated into catalyst, and the vapour product from every riser reactor, except the last, is suitably fed to the subsequent riser reactor. Obviously a larger amount of oxygenation catalyst then needs to be added to the inlet end of the subsequent riser reactors. The separated catalyst can be collected in one or more shared collection vessels, and (full or partial) regeneration can occur in one or more shared regenerator units.

The olefin-containing product stream in line 52 is preferably at least partially recycled as olefinic co-feed to the inlet of the first reactor, line 38. Preferably this is done after one or more fractionation steps, to isolate an optimised olefinic co-feed composition from the olefin-containing product, and to obtain a desired product stream such as a stream or streams comprising predominantly ethylene and propylene. Preferred compositions of the olefinic co-feed have been discussed hereinbefore.

Figure 1 shows schematically a separation system 70 for example including one or more distillation columns, fractionating the olefin-containing product stream 52 into a light fraction 73 comprising light contaminants, such as carbon monoxide, carbon dioxide, methane; a light olefinic product fraction 74 comprising for example ethylene and optionally propylene; a middle fraction 76 comprising e.g. C4 olefins; and one or more heavy product fractions, e.g. fractions with hydrocarbons with 5, 6 or 7+ hydrocarbons, in line 78. Also an outlet line 79 for withdrawing a water-rich fraction is provided. The middle fraction 76 can suitably be recycled to line 38.

Reference is made to Figure 2, showing a second embodiment of the present invention. Like reference numerals as in Figure 1 are used for the same or similar parts of the serial riser reactor system 101. It suffices to discuss the differences and additions. Instead of a third riser stage with a single riser, the third riser stage 128 comprises two parallel risers 13a, 13b.

In view of the increasing catalyst and vapour flow through subsequent stages of the reactor system, the last riser stage is first likely to be limited by engineering considerations of large diameter risers. Splitting up the last stage into two parallel risers as in this example solves this problem. For even higher throughputs through the reactor system, also earlier stages can be formed of parallel riser arrangements, and more than two risers, such as 2,4,5,6 or more, can be arranged per stage.

Each riser 13a,13b has at its lower end an inlet end 18a,18b with one or more inlets, and at its upper end an outlet end 23a,23b with one or more outlets. The conduit 30 from the outlet 29 of the second riser 12 is in fluid communication with both inlet ends 18a,18b of the third riser reactors 13a, 13b. Preferably, the two riser reactors have substantially the same diameter and height, and each riser reactor receives substantially the same portion of the effluent from the second riser 12. By substantially is meant within 20%, preferably within 10%. Likewise, outlet 29 of the second riser 12 is connected via a conduit 30 to the inlet end 18 of the third riser 13.

Oxygenation catalyst is also added to both riser reactors. As shown in the drawing, oxygenation catalyst is added to the total effluent from riser 12 in line 30, before the combined effluent and oxygenation catalyst is fed to the riser reactors 13a, 13b via lines 130a, 130b. Alternatively, oxygenation catalyst is added separately for each riser reactor after the effluent from the second riser reactor has been split, or the catalyst can alternatively be added to the inlet ends 18a,b directly.

Both risers 13a,13b are arranged to receive oxygenate at their inlet end, via conduits 36a,b which are both connected to oxygenate feedstock line 37.

The outlets from the last riser reactors 13a,13b are in this embodiment combined and connected to the common collector and vapour/solids separator unit 50 via lines 51a,51b, 151. The unit 50 can also be integrated with the outlet end of one or both of last stage risers.

Parallel riser reactors are for example described in WO 01/85872, WO 2004/31327 and WO 2004/37950.

It shall be clear that in other embodiments also other riser stages but the last can be formed of a plurality of parallel riser reactors. It is possible but not needed that all riser reactors of a previous stage communicate with all riser reactors of subsequent stages. The system can also form several branches. By counting in upstream direction the riser reactor stages with which a selected riser reactor is in fluid communication, plus 1, the number of the stage to which the selected riser reactor belongs can be determined.

Reference is now made to Figure 3, showing a further embodiment of the present invention. This embodiment includes a pre-reactor for converting alkylalcohol such as methanol to dialkylether, such as dimethylether. In the Figure a vaporous alkyl alcohol is passed via a line 151 through coolant tubes in a dialkylether reactor 1522. As the formation of dialkylether from alkyl alcohol is exothermic, the vaporous alkyl alcohol is heated and the thus heated alkyl alcohol leaves the reactor as hot effluent via a line 153. The hot effluent is subsequently recycled to the reactor 152 but at the reaction side of the coolant tubes. The stream from line 151 and the one from line 153 are passed co-currently through reactor

152. In reactor 152 the alkyl alcohol is converted to dialkylether and water in contact with a suitable catalyst, e.g. gamma-alumina. A dialkylether product stream comprising dialkylether, water and alkyl alcohol leaves the reactor via a line 154. The hot dialkylether product stream may be cooled before being passed on to a separation section 155. The stream may be cooled in one or more stages, e.g., by indirect heat exchange and/or by flashing in a flash vessel wherein the pressure is reduced and the product stream is cooled (not shown). In the separation section 155, here depicted as a fractionation column, the dialkylether product stream is separated into a liquid stream 156 comprising water and preferably less than 1%wt alkyl alcohol, based on the total of water and alkyl alcohol, and a vaporous dialkylether-rich stream 157, comprising dialkylether, the majority of the alkyl alcohol and typically some water. The stream in line 157 is in this embodiment the oxygenate feedstock to the process of the present invention, and it will be understood that the following description of the embodiment of the serial riser reactor system is independent of the combination with this oxygenate feedstock prereactor. The oxygenate feedstock stream 157 may be split into several portions. In the case of the present Figure 3 there are two portions, but it will be evident that when more portions are desired in view of the number of reactors the number can be adapted. The portion in line 158 is fed to a first riser reactor 160 of a serial riser reactor system, whereas the portion in line 159 is fed to a second riser reactor 170 of the serial riser reactor system. The stream in line 158 may be further heated (not shown), e.g. by additional heat exchange or other heating means. The stream is combined

with a stream of an olefinic co-feed, comprising olefins with e.g. 4 and/or 5 carbon atoms which stream is provided via a line 177.

In the riser reactor 160 the streams from lines 158 and 177 are contacted with a suitable catalyst, provided via a line 166, and the formed combination of oxygenate, olefin, water and catalyst is passed upwards and this combination leaves the riser reactor 160 via a line 161 as reaction product.

The lines 158 and 177 are shown as combined before entering the riser reactor 160, but it will be understood that each may debouch into riser reactor 160 separately. Alternatively, line 166 is shown as a separate line, but it will be understood that it may be combined with any of the two other lines 158 and 177 before entering the riser reactor 160.

Via line 161 the reaction product is passed to a separation means, e.g. a cyclone 162, from which catalyst particles are discharged via a line 163 and passed to a catalyst buffer vessel 165, and from which the vaporous reaction product, comprising dialkylether, olefins and water is withdrawn via line 164. This vaporous product in line 164 is combined with the portion of the dialkylether-rich feed in line 159 and passed to the second riser reactor 170, in which a similar reaction takes place as in riser reactor 160. Catalyst for riser reactor 170 is provided via line 167. The reaction product of the riser reactor 170 is discharged therefrom via line 171 and passed to a separation means 169, e.g. a cyclone. In the separation means catalyst particles are separated from the vaporous products and withdrawn from the separation means 169 via a line 168 and passed to the catalyst buffer vessel 165.

It will be realised that at the dialkylether conversion reaction some coke formation may take place, which coke may deposit on the catalyst particles. Therefore, it is advantageous to regenerate the catalyst particles periodically. Conveniently this may be achieved by continuously or periodically withdrawing part of the catalyst inventory of the catalyst buffer vessel 165 and passing it to a regeneration vessel (not shown), where typically coke is burned partially or substantially fully at temperatures of about 600 °C or more. The size of the portion sent to the regeneration vessel depends on the average degree of deactivation or coking, and on the regeneration conditions, e.g. partial or full burning of coke. The regenerated catalyst particles are recycled to the catalyst buffer vessel or to the riser reactor(s) directly. The regeneration is not shown in the Figure.

As product from the separation means 169 an olefins-containing product stream is obtained in a line 172. This product is passed to a fractionation section, in the Figure represented by a column 173 in which the olefins-containing product stream is separated into a light fraction 174, comprising light contaminants, such as carbon monoxide, carbon dioxide and methane, into an ethylene fraction 175, into a propylene fraction 176 and into a C4 olefin fraction 177. Optionally, one or more heavier fractions, e.g. fractions with hydrocarbons with 5, 6 or 7+ hydrocarbons may be withdrawn separately from the column 173 (not shown). The separation section also includes a line 178 for withdrawing water. The light fraction in line 174 is discharged, e.g., combusted as fuel. Ethylene and propylene are recovered as products. Water in fraction 178 is withdrawn, and the C4 fraction is recycled via line 177 to the dialkylether-rich stream in line 158.

Figure 3 shows two riser reactors. It will be evident to the skilled person that more than two, e.g., 3 or 4, riser reactors may be used.

Examples

As examples, results from model calculations of various reactor systems are presented hereinbelow. The calculations were based on a kinetic reaction network 190 depicted in Figure 4. This reaction network represents the alkylation and cracking of C2-C7 olefins, in the presence of oxygenates comprising dimethylether (DME) and methanol (MeOH). The reaction conditions are such that higher than C7 olefins are hardly formed and can be neglected. In the alkylation it is assumed that DME reacts with an olefin, producing methanol, and that 2 methanol molecules are dehydrated to DME. Water is being obtained as a reaction product from alkylation. This cycle is indicated in Figure 4 for the alkylation from ethylene to propylene, and it shall be clear that it also applies to the alkylation steps of C3= and higher olefins. C2-C4 olefins are not cracked under the prevailing operating conditions. Cracking of one C5= molecule results in one C2= and one C3= molecule, cracking of C6= in two C3= molecules, and cracking of C7= in one C3= and one C4= molecule. This is illustrated by the arrows 192, 193, 194.

On the basis of the reaction network 190 a kinetic model was established, and parameters of the model were determined based on experiments of oxygenate (DME and/or MeOH) and various olefin feed conversions over ZSM-23. The kinetic model was then used in various reactor models as discussed below. Aspen Custom Modeller was used in this process, together with proprietary software routines.

The model does not take into account the production or conversion of paraffins. It is known that some paraffins are being formed over a zeolite catalyst. One of the options of practical interest is the recycle of C4= olefins from the reaction product to the inlet of the reactor system. It is known that separating C4 olefins from C4 paraffins is difficult, and may not be economically attractive. Therefore the recycle stream may contain C4 paraffins (C4,0) together with C4=. In some Examples below, the role of C4 paraffins has been included. In order to mimic their production in the process, a small amount was included in the oxygenate feed, and a corresponding bleed stream was taken out of the product fraction. The net effect is a level of C4,0 in the process, which is further assumed to be inert.

Example 1

Model calculations for a reactor system 201 comprising three sequential isothermal plug flow reactors have been conducted, which can be regarded as an approximation of a serial riser reactor system according to the invention. The reactor system 201 is depicted in Figure 5, comprising three sequential isothermal reactors 211,212,213, in fluid communication via lines 228 and 230. In the calculations, oxygenate feedstock (DME, MeOH) was fed via lines 234,235,236, and C4 olefin was fed to the first reactor 211 via line 238. Products (ethylene, propylene and water) are withdrawn after separation of C4 olefins from the olefinic effluent in line 251 in separation system 270, as generally depicted by line 274. The majority of C4=, together with the majority of C4,0, is recycled to the first reactor 211 via line 238.

The catalyst amount assumed in the model was 5,7.5 and 12.5 tonnes for the reactors 211, 212, 213, respectively. 40 wt% of the catalyst was assumed to be zeolite. A uniform temperature of 522 °C and pressure of 1 bar was assumed. In an isothermal model it is not needed to consider the actual flow of catalyst through the system, therefore no catalyst separation and addition is shown.

The composition of various streams indicated by the reference numerals of Figure 5 are given in Table 1.

Table 1

Stream (kmol/h)	238	234	228	235	230	236	251
DME	0	922	0	922	0	922	0
MeOH	0	326	0	326	1	326	1
H_2O	0		1248		2495		3743
$C_2^=$	0		355		794		1194
$C_3^=$	0		985		1134		1309
$C_4^=$	806		426		630		849
C_4^0	418	22	440		440		440
$C_5^=$	0		6		11		5
$C_6^=$	0		0		0		0
$C_7^=$	0		0		0		0
Total	1224	1270	3459	1248	5505	1248	7540
Total (t/h)	69	54	124	53	176	53	229

A high selectivity for ethylene is observed in this staged reactor line-up, the molar ratio of C2=/C3= obtained is 0.91.

Comparative example 2

Model calculations for a reactor system 301 comprising a single isothermal plug flow reactor, not according to the invention, have been conducted for comparison. The reactor system 301 is depicted in Figure 6, comprising a single isothermal reactor 311, oxygenate feed line 334, and C4 olefin fed feed/recycle line 338. Products (ethylene, propylene and water) are withdrawn after separation of C4 olefins from the olefinic effluent in line 351, in separation system 370, as generally depicted by line 374. The majority of C4= and C4,0 is recycled.

The catalyst amount assumed was 12.5 tonnes for the reactors 311, 40 wt% of which being zeolite. A uniform temperature of 522 °C and pressure of 1 bar was assumed.

The composition of various streams indicated by the reference numerals of Figure 6 are given in Table 2.

Table 2

Stream (kmol/h)	Recycle 338	Feed 334	Products 328
DME		2766	0
MeOH		978	1
H_2O			3743
$C_2^=$			674
$C_3^=$			1646
$C_4^=$	897		944
C_4^0	418	22	440
$C_5^=$			7
$C_6^=$			0
$C_7^=$			0
Total	1315	3766	7455
Total (t/h)	74	160	234

A much lower ethylene selectivity than in the staged reactor system of Example 1 is observed. The C2=/C3= molar ratio in the product is only 0.41.

Example 3

The calculations according to Example 1 were repeated, but now the temperature profile in the reactor was taken into account. The alkylation reaction is exothermic and proceeds primarily in the upstream part of each reactor. The cracking reaction is endothermic and proceeds primarily in the downstream part. The overall reaction is exothermic. Therefore, the temperature along each reactor increases downstream the inlet end to some maximum, and decreases again to an outlet temperature somewhat higher than the inlet temperature. The overall temperature rise from the inlet temperature 522 °C is modest, in the order of 5-15 degrees, and the maximum is below 550 °C in the examples considered. The assumption of an isothermal reactor can therefore be justified. Including the temperature considerations, a molar C2=/C3= ratio in the product of 0.88 was determined. In view of the relatively modest temperature rise, one can adjust or control the inlet temperature of each stage by adjusting the feed temperature, in particular the oxygenate feed temperature. Feeding cooler oxygenate can be sufficient to compensate for the increased temperature of effluent from the previous riser and additional catalyst from regeneration, so that a predetermined combined inlet temperature is achieved.

Example 4

As further example according to the present invention, model calculations for a reactor system comprising three sequential risers in a configuration according to Figure 1 are presented. Reference numerals of Figure 1 are used to designate the various system components and streams. The risers 11,12,13 have equal height and increasing diameters. The oxygenate feed via line 34 to the first riser consists of 17.3 kmol/h dimethylether (DME), 6.1 kmol/h methanol (MeOH), and 0.4 kmol/h C4 paraffins. Further, an olefinic co-feed of 16.4 kmol/h C4 olefins and 7.8 kmol/h C4 paraffins is added via line 38. These data are also given in the columns for lines 34 and 38 in Table 3. 50910 kg/h of catalyst are fed through line 40. The catalyst was assumed to contain 40% of oxygenation zeolite.

The effluent from riser 11 in line 28 comprises, in addition to the catalyst, reaction products as shown for line 28 in Table 3. The entire effluent from riser 11, including the catalyst, is fed to the riser 12. Additional oxygenate feed is added via line 35, as shown in Table 3, and 25760 kg/hr catalyst is added via line 41.

The effluent from riser 12 in line 30 comprises, in addition to the catalyst, reaction products as shown for line 30 in Table 3. The entire effluent from riser 12, including the catalyst, is fed to the riser 13. Additional oxygenate feed is added via line 36, as shown in Table 3, and 48920 kg/hr catalyst is added via line 42.

In the calculations, moreover the temperature profile along the reactors and the pressure distribution was taken into account.

The composition of the reaction product in line 51 is also shown in Table 3. All of the olefinic co-feed 38 is obtained as a fraction from the reaction product. From the ethylene and propylene concentration in the reaction product, a high molar ratio of ethylene to propylene of 0.82 can be calculated. Also with this more extended model, a high selectivity of the reaction towards ethylene, for example when compared to Example 1, is observed.

Table 3 only shows the main components of the reactor effluents. Table 4 lists the concentrations of minor by-products not listed in Table 3 in the effluent 51, totalling about 12 wt% of the reaction product.

Table 3

Line ->	38	34	28 (excl. cat.)	35	30 (excl. cat.)	36	51 (excl. cat.)
DME	0	17	0	17	0	17	0
MeOH	0	6	0	6	0	6	0
H2O	0		23		47		70
C2=	0		7		14		21
C3=	0		19		22		26
C4=	16		9		13		17
C4,0	8	0	8	0	8	0	8
C5=	0		0		0		0
C6=	0		0		0		0
C7=	0		0		0		0
T (C)	522	341	528	293	531	52	528

Table 4

By-products	kmol/h
CO+CO2	0.4
C1	0.8
other C2 species	0.1
other C3 species	1.0
other C4 species	0.4
other C5 species	0.9
other C6+ species	0.5

Table 3 also shows the temperatures of the various streams. The temperature of the catalyst in lines 40,41,42 is taken as 532 degrees C. This is a few degrees higher than the temperature of the effluent 51, since part of the catalyst undergoes regeneration at higher temperatures. The temperature of the recycle stream 38 is selected at 522 degrees C. The overall reaction in each riser reactor is exothermic. The temperature of the oxygenate feed to each riser is set individually, so as to provide substantially the same reactor inlet temperature for each of the sequential riser reactors after combining the various feed, catalyst and product components. Heat exchangers (not shown) can be arranged in each of the lines 34,35,36 to allow setting of a desired oxygenate feed temperature by heating or cooling.

Alternatively or in addition, the temperatures of the catalyst feeds 40,41, 42 and/or of the recycle stream 38 could be controlled.

The claims defining the invention are as follows:

1. A process for converting an oxygenate to an olefin-containing product, wherein oxygenate is contacted with an oxygenate conversion catalyst, to convert the oxygenate to an olefin –containing product, which contains ethylene and propylene with a molar ethylene/propylene ratio of at least 0.5, in a reactor system comprising two or more serially arranged riser reactor stages to obtain a riser reactor effluent from each stage, wherein each riser reactor stage comprises a single riser reactor or a plurality of parallel riser reactors, such that at least part of the riser reactor effluent of a preceding riser reactor stage is fed into a subsequent riser reactor stage, and wherein oxygenate is added to a plurality of the riser reactor stages.

2. The process according to claim 1, wherein the mass flow rate of oxygenate conversion catalyst in each subsequent riser reactor stage, after the first, to which oxygenate is added is higher than in the preceding riser reactor stage.

3. The process according to claim 1 or 2, wherein the cross-section of the last of the two or more serially arranged riser reactor stages is larger than the cross-section of the first, in particular wherein the cross-section of each subsequent riser reactor stage to which oxygenate is added, after the first, is higher than that of the preceding riser reactor stage.

4. The process according to any one of claims 1-3, wherein the riser reactor effluent of a preceding reactor stage comprises gaseous effluent and solid oxygenate conversion catalyst, and wherein at least 50 wt% of the gaseous effluent is fed to the subsequent riser reactor stage, preferably wherein also at least 50 wt% of the solid oxygenate conversion catalyst is fed to the subsequent riser reactor stage, more preferably wherein substantially all riser reactor effluent is fed to the subsequent riser reactor stage.

5. The process according to any one of claims 1-4, wherein the gaseous effluent from the last riser reactor stage, preferably each gaseous effluent from one of the riser reactors, has an oxygenate concentration below 10 wt%, preferably below 5 wt%, more preferably below 2 wt%.

6. The process according to any one of claims 1-5, wherein an olefinic feedstock is added to the first riser reactor stage.

7. The process according to claim 6, wherein the olefinic feedstock during normal operation is at least partially obtained from one of the riser reactor effluents.

8. The process according to any one of claims 1-7, wherein the oxygenate conversion catalyst comprises a one-dimensional molecular sieve having 10-membered ring channels, preferably at least one of a zeolite of the MTT-type and/or of the TON-type.

9. The process according to claim 8, wherein the oxygenate conversion catalyst comprises more than 50 wt%, preferably at least 65 wt%, based on total molecular sieve in the oxygenate conversion catalyst, of the one-dimensional molecular sieve having 10-membered ring channels.

10. The process according to claim 8 or 9, wherein the oxygenate conversion catalyst comprises at least 1 wt%, based on total zeolite in the oxygenate conversion catalyst, of a further zeolite having more-dimensional channels, preferably at least 5 wt%, more preferably at least 8 wt%.

11. The process according to claim 10, wherein the catalyst composition comprises less than 35 wt% of the further molecular sieve, based on the total weight of molecular sieves in the catalyst composition, preferably less than 20 wt%, more preferably less than 18 wt%, still more preferably less than 15 wt%.

12. The process according to claim 10 or 11, wherein the further molecular sieve is a MFI-type molecular sieve, in particular zeolite ZSM-5.

13.. A reactor system comprising two or more serially arranged riser reactor stages including a first and at least one subsequent riser reactor stage, wherein each riser reactor stage comprises a single riser reactor or a plurality of parallel riser reactors and has a total cross-sectional area, wherein an inlet of a selected riser reactor of a subsequent stage is in fluid communication with an outlet of a riser reactor of a preceding stage, and wherein the first of the two or more serially arranged riser reactor stages has a smaller total cross-sectional area than at least one of the subsequent riser reactor stages.

14. The reactor system according to claim 13, wherein each riser reactor stage comprises a single riser reactor.

15. The reactor system according to claim 13 or 14, wherein at least the first riser reactor stage comprises a single riser reactor, and wherein at least the last riser reactor stage comprises a plurality of parallel riser reactors.

16. A process for converting an oxygenate to an olefin-containing product comprising the steps substantially as herein described with reference to the examples and/or accompanying drawings.

17. A reactor system comprising two or more serially arranged riser reactor stages substantially as herein described with reference to the examples and/or accompanying drawings.

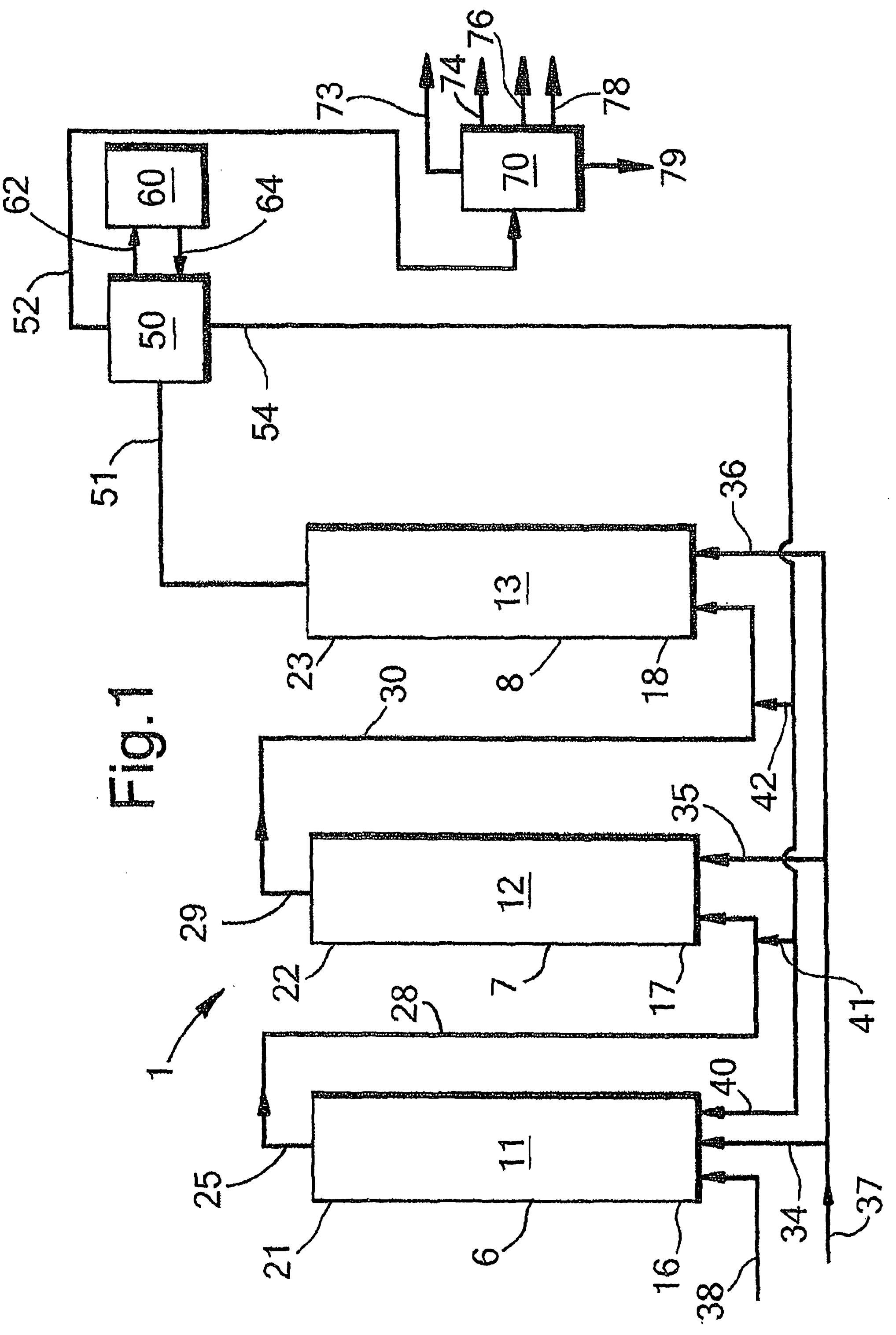
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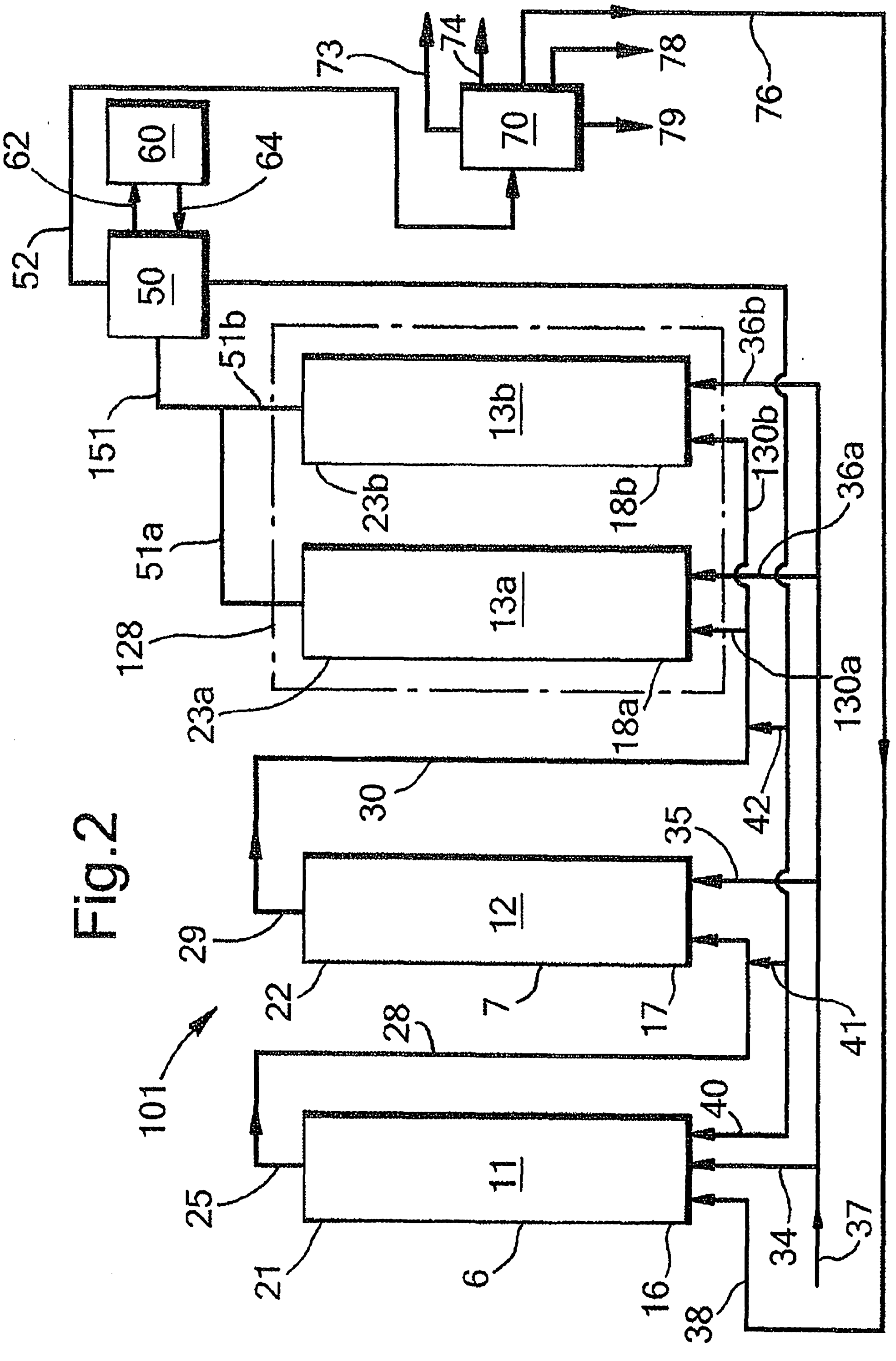
Fig.1

Fig.2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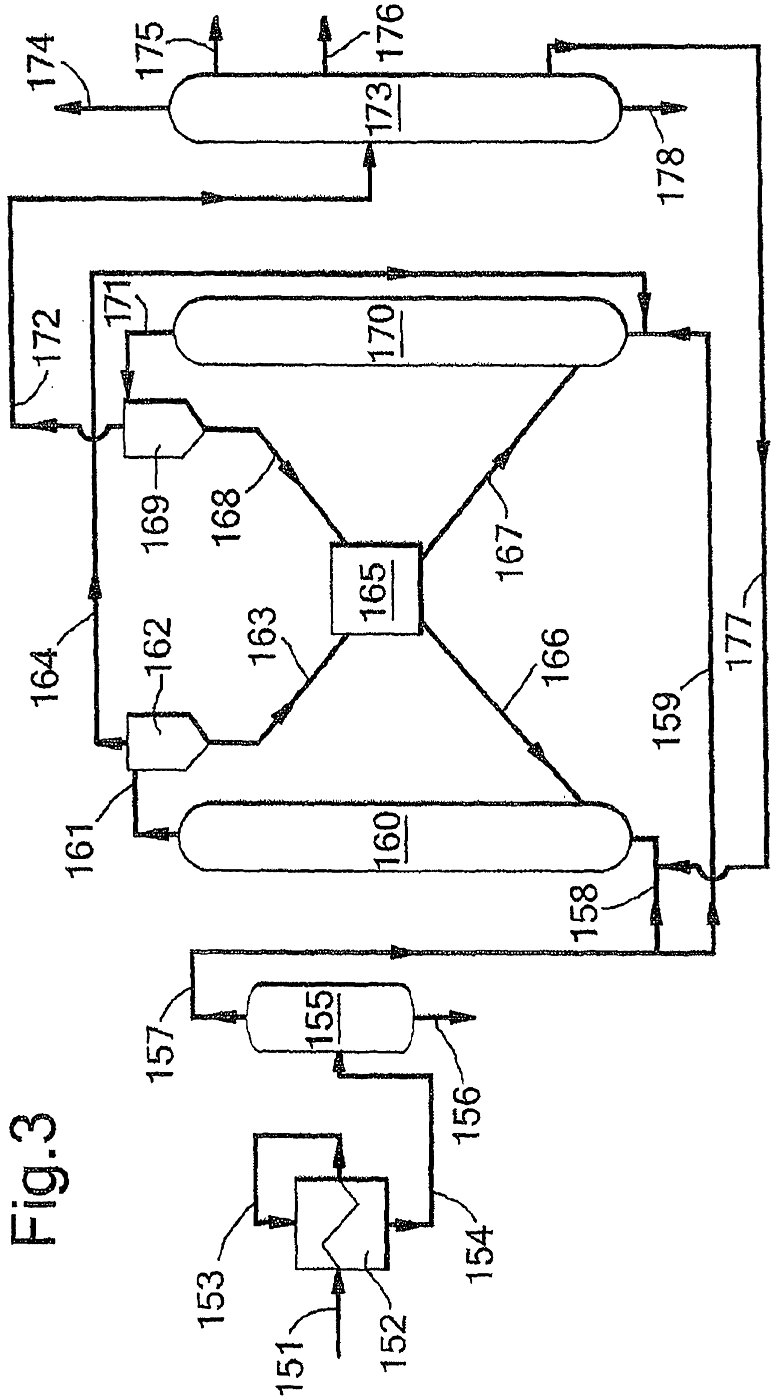
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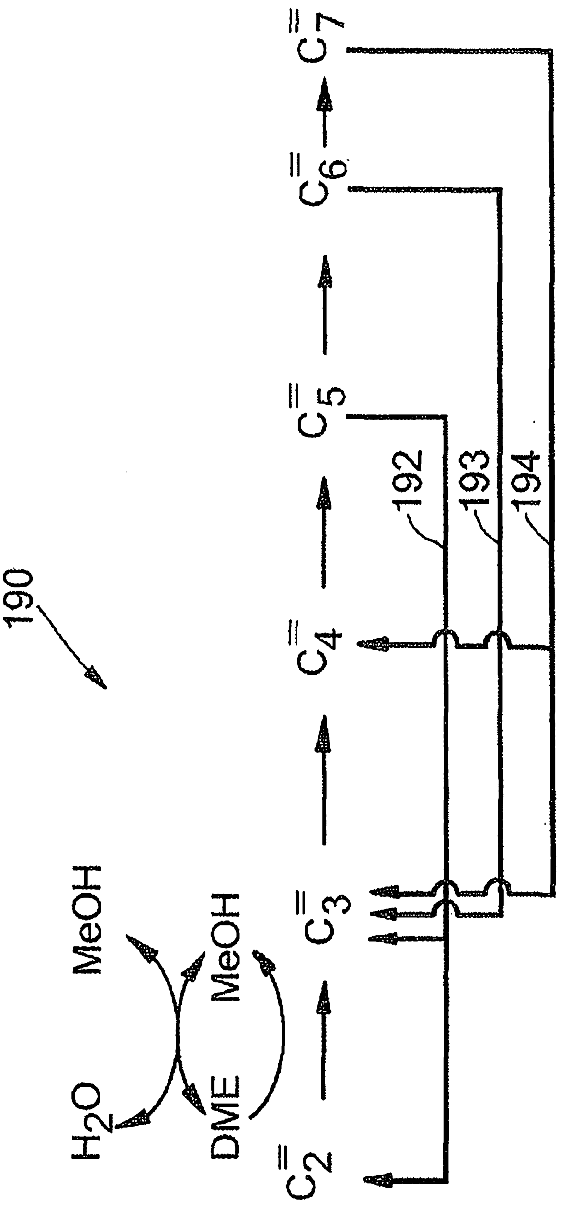
Fig.3

Fig.4



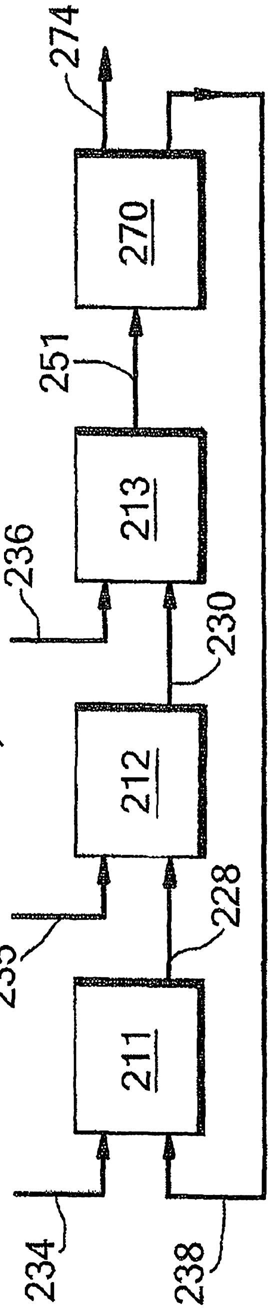

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Fig.5

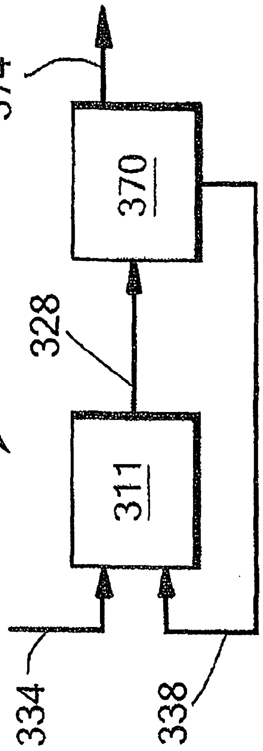
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Fig.6