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(54) Title: PROCESS FOR PRODUCING SHORT-CHAIN OLEFINS WITH PROLONGED CYCLE TIME

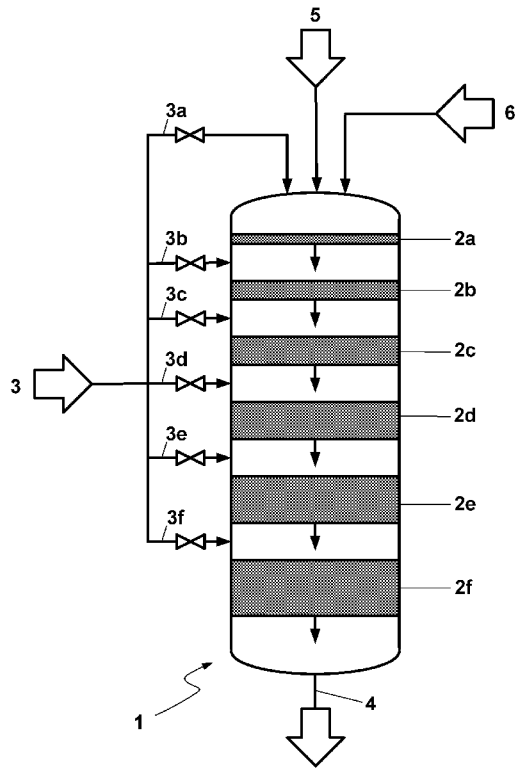

Fig. 1

(57) Abstract: There is proposed a process for producing short-chain olefins by conversion of oxygenates in a multi-stage fixed-bed reactor, in which the individual stages or reaction zones are covered with beds of a granular, form-selective zeolite catalyst and the feed mixture containing oxygenates is added distributed over the reaction stages. An increase of the availability of the fixed-bed reactor for the olefin production with the same or an increased yield of short-chain olefins is achieved in that one or more reaction zones are charged with a distinctly reduced mass flow of the feed mixture containing oxygenates, wherein the reduced mass flow fraction is distributed over the other reaction zones.

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Process for Producing Short-Chain Olefins with Prolonged Cycle Time

Field of the Invention

This invention relates to a process for producing a hydrocarbon product containing short-chain, low-molecular olefins, in particular ethylene and propylene, by conversion of an educt mixture containing steam and oxygenates, for example methanol and/or dimethyl ether (DME), in a multi-stage fixed-bed reactor. The individual stages or reaction zones of the fixed-bed reactor are covered with beds of a granular, form-selective zeolite catalyst. It is the objective of the process according to the invention to increase the availability of the fixed-bed reactor for the olefin production with the same or an increased yield of short-chain olefins, in particular of propylene (propene), as compared to previously known processes of the same type and thus increase the space-time yield of the reactor with regard to the olefins, in particular with regard to the propylene production.

Prior art

The production of hydrocarbon mixtures, in particular also of short-chain olefins, by conversion of oxygenates by using form-selective molecular sieve catalysts, in particular of pentasil zeolites of the structure type ZSM-5, is known from the prior art and described for example in the European Patent Application EP 0448000 A1 and the European Patent Specification EP 1289912 B1. The use of multi-stage fixed-bed reactors for this purpose also has been described already. For example, the International Patent Application WO 96/15082 A1 teaches a process for converting a feed mixture containing oxygenate compounds, for example methanol or dimethyl ether, into gasoline-like hydrocarbon compounds in a multi-stage fixed-bed process. In this process, fresh feed material containing oxygenates is supplied to a reaction zone together with the product gas from a preceding reaction zone and additional dilution gas. The temperature and composition of the dilution gas is chosen such that the increase in temperature in the exothermal reaction of the oxygenates to hydrocarbons in each of the succeeding reaction

zones is limited to a maximum of 150 °C, wherein the steam partial pressure should not exceed 2.2 ata. In this way, a premature deactivation of the zeolite catalyst used should be prevented, since too high a steam partial pressure at too high temperatures leads to an irreversible change in structure of the zeolite, with which catalytically active centers get lost. On the other hand, the steam is required as dilution medium and to prevent excessive carbon deposits on the catalyst. A slow deposition of carbon on the catalyst during the synthesis operation, however, is inevitable. When the same exceeds a tolerable maximum, the production operation must be interrupted and the carbon deposits must be removed for example by controlled burning off. The catalytic activity of the catalyst thereby can largely be restored, i.e. regenerated. The regeneration of the catalyst can be repeated several times, until the above-described irreversible deactivation has decreased the catalytic activity so much that a further use of the catalyst is prohibited for economic reasons. The time interval with production operation of the catalyst between two regenerations is referred to as cycle or also reaction cycle. The first cycle is the operating phase between the restart of the reactor with newly produced catalyst and the first regeneration.

The International Patent Application WO 2007/140844 A1 relates to a reactor for producing C_2 to C_8 olefins, preferably propylene, from a feed mixture comprising gaseous oxygenate, preferably dimethyl ether (DME) and/or methanol, steam and one or more of the hydrocarbons, which has a temperature of 400 to 470 °C, and to a method for operating the reactor. The reactor contains a plurality of reaction stages or reaction zones arranged inside a closed upright container, which are traversed by the material stream from the top to the bottom, each consisting of a supporting tray with a fixed-bed zone located thereon, which is formed of a bed of granular molecular sieve catalyst. In a particular configuration, the reactor contains six reaction zones. Each supporting tray is constructed of cells firmly connected with each other, which are arranged one beside the other without spaces, and is suspended freely in the container. The cells are filled with a layer of molecular sieve catalyst. In the space defined by two adjacent reaction zones at the top and at the bottom, an atomizer system each is provided in the form of a number of nozzle tubes for uniformly spraying a liquid phase containing DME and/or methanol, chiefly consisting of steam and having a temperature of 25 to 150 °C by means of a gas

phase saturated with water, chiefly containing DME and/or methanol and having a temperature of 170 to 300 °C towards the reaction stage following next in downstream direction. By spraying the liquid phase, the temperature of the reaction mixture exiting from the reaction stage with a temperature of 400 to 500 °C is lowered to a value of 380 to 470 °C, so that the reaction proceeds in a narrow temperature range (quasi isothermally). The liquid phase can contain up to 30 vol-% of DME and/or methanol and the gas phase can contain up to 80 vol-% of DME and up to 30 vol-% of methanol.

For operating the reactor, a feed mixture containing gaseous oxygenate, preferably DME and/or methanol, as well as steam, which has a temperature of 150 to 300 °C, is cooled to a temperature of 100 to 160 °C, separated into a liquid phase and a gas phase, and liquid phase and gas phase are divided into several partial streams whose number each corresponds to the number of the spaces existing between the reaction stages. Based on a space, a gas-phase partial stream after heating to a temperature of 170 to 300 °C and a liquid-phase partial stream after cooling to a temperature of 25 to 150 °C each is supplied to an atomizer and sprayed into the space. By supplying gas and liquid in a corresponding temperature and quantity between the individual reaction stages, the inlet temperature of the reaction mixture exiting from the reaction stage into the space can be adjusted to the desired temperature before entry into the next following reaction stage.

The features of the reactor described in the document WO 2007/140844 A1 according to claims 1 to 13 as well as the features of the method for operating the reactor according to claims 14 to 15 and furthermore the description of an exemplary embodiment according to Fig. 1 to Fig. 7 and the associated description of Figures on p. 5 to p. 8 herewith are incorporated into the disclosure of the present patent application by reference.

The International Patent Application WO 2010/066339 A1 teaches a process for producing a product containing propylene and ethylene by converting methanol and ethanol at the same time in an adiabatic reactor containing a plurality of series-connected reaction zones, wherein each reaction zone is covered with a fixed bed of form-selective catalyst, in that a feed mixture, comprising gaseous methanol, DME, steam and possibly one or

more C_2, C_4, C_5, C_6, C_7, C_8 olefins and paraffins, is charged at least to the first reaction stage of the reactor at temperatures of 300 to 600 °C and pressures of 0.1 to 20 bar, absolute. By the distributed addition of the feed mixture containing oxygenates, advantages are achieved with regard to the temperature control and the suppression of undesired consecutive and side reactions.

With reference to the prior art discussed above, it can clearly be seen that so far it has been the primary objective to design the process of producing short-chain olefins from oxygenates by means of a multi-stage reactor such that optimum yields are obtained for the target products, i.e. in particular ethylene and propylene, with a good control of the exothermicity of the conversion reaction, since a maximization of the yield represents an important parameter for optimizing the process economy. What has been considered less, however, is the influence of the duration of the reaction cycles on the economy of the production process.

The catalyst life achieved so far with the production processes known from the prior art as described above is regarded as comparatively short - in particular with regard to the considerable price of the catalyst. Furthermore, several regenerations are required to achieve this previous maximum catalyst life.

Carrying out the regeneration between the various reaction cycles leads to a reduction of the operating period per reactor and per operating year and to an increased consumption of operating materials. This applies in particular to production plants which are operated outside an integrated association with ancillary facilities supplying operating materials. Carrying out each individual step of the regeneration procedure and transferring the reactor from the operating state into the regeneration mode and back binds a considerable part of the operating costs in the plant. In addition, the reactor is not available for the olefin production during the regeneration, so that the maintenance of a continuous production operation requires a multi-strand concept for the production plant. Therefore, an increased catalyst life and an increase in the number of reaction cycles (tantamount to a reduced number of regenerations) would considerably improve the process economy of the production of short-chain olefins from oxygenates.

Description of the Invention

The object of the present invention therefore consists in providing a process for producing short-chain, low-molecular olefins, such as ethylene and in particular propylene, from oxygenates such as methanol or DME, in which the length of the reaction cycles can be increased as compared to the processes known from the prior art, without suffering losses as regards the yields of the target products.

The aforementioned object is solved with the invention according to claim 1 with a process for producing a hydrocarbon product containing olefins, comprising ethylene and propylene, by converting an educt mixture comprising steam and oxygenates, such as methanol and/or dimethyl ether, which is divided into several partial streams, to olefins under oxygenate conversion conditions in a reactor with a plurality of series-connected reaction zones which are in fluid connection with each other, comprising a first reaction zone and at least one succeeding reaction zone, wherein the first reaction zone is charged with an educt mixture partial stream and steam as well as optionally recirculation streams, and the succeeding reaction zones are charged with an educt mixture partial stream and the succeeding reaction zones additionally are charged with the product stream of the upstream reaction zone, which is characterized in that at least one of the succeeding reaction zones is charged with a reduced educt mixture partial stream which is smaller than the educt mixture partial stream supplied to the upstream reaction zone.

Fluid connection between two reaction zones is understood to be any kind of connection which enables a fluid, for example the feed stream, to flow from the one to the other of the two regions, regardless of any interposed regions or components.

Short-chain olefins in accordance with the present invention in particular are understood to be olefins which under ambient conditions are present in gaseous form, for example ethylene, propylene as well as the isomeric butenes 1-butene, cis-2-butene, trans-2-butene, iso-butene. Oxygenates are understood to be all oxygen-containing organic compounds which in the process according to the invention can be converted into olefins.

The conversion conditions required for the conversion of oxygenates to olefin products are known to the skilled person from the prior art, for example from the documents discussed above. Necessary adaptations of these conditions to the respective operating requirements will be made on the basis of routine experiments.

Further advantageous aspects of the process according to the invention can be found in sub-claims 2 to 12.

The idea underlying the present invention is based on varying the distribution of the educt mixture, i.e. the fresh oxygenate feed, to the catalyst zones of a multi-stage olefin synthesis fixed-bed reactor, in which all catalyst zones are filled with a catalyst active for the olefin synthesis from oxygenates, for example a ZSM-5 zeolite catalyst. For this purpose, the supply of the educt mixture is shifted from the last catalyst zones towards the front catalyst zones and thus the uniform distribution of the educt mixture partial streams, as it is taught in the prior art, is eliminated. Accordingly, the loading of the front catalyst zones with fresh oxygenate feed is significantly higher and the effective time of contact with the oxygenate feed is reduced. One or more of the succeeding catalyst zones are charged with a significantly reduced educt mixture partial stream. In the extreme case, for example, the last catalyst zone in flow direction is not charged with fresh feed, but only with the product stream of the upstream catalyst bed.

It has been found that with this new supply of the educt mixture not only the methanol conversion is increased, but also the propylene yield is not negatively influenced. The methanol conversion is connected with the duration of a reaction cycle such that as the end of a reaction cycle that point in time is defined at which a predefined minimum methanol conversion is reached or fallen short of. When reaching this point in time, it is necessary to transfer the reactor into the regeneration mode. These findings are surprising and in contrast with the expectation of the skilled person, according to which a rather uniform distribution of the educt mixture to all catalyst zones should lead to a uniform load of the catalyst and thus also to a uniform deactivation of the catalyst beds incorporated in the individual zones.

The increased methanol conversion observed when supplying the educt mixture according to the invention allows to extend the duration of the production operation per reaction cycle, before a regeneration becomes necessary. Accordingly, the frequency of the required regenerations is reduced. Surprisingly, it has been observed that the total amount of carbon deposited in the reactor remains approximately constant despite a changed supply of the educt mixture. Therefore, the same regeneration procedure can be employed, and the duration and costs per regeneration remain unchanged. Hence it follows that the influence of the regeneration costs on the produced ton of product, for example propylene, is decreased by the application of the process according to the invention.

The reduced amount of regeneration cycles per year of operating period simplifies the plant operation, since the procedures for the transfer of the reactors from the production operation into the regeneration mode and back must be performed less often. This also has additional advantages with regard to the service life of the catalyst used, since the performance of each regeneration is connected with a thermal load which leads to an irreversible deactivation - on a minor scale per regeneration. Since the irreversible deactivation of the catalyst ultimately determines its useful life, i.e. the possible operating period up to the necessary replacement of the catalyst filling of the synthesis reactor, the extended duration of the reaction cycles consequently also leads to an extension of the catalyst life.

In principle, the effect described above can be caused in that by charging with a reduced educt mixture partial stream, the space velocity in the corresponding catalyst zone or zones is reduced considerably as compared to the catalyst zones arranged further upstream. A particularly large effect is obtained when the corresponding educt mixture partial stream or streams not only are reduced, but decreased to zero.

The change of the supply of the educt mixture according to the invention advantageously also can be used to postpone the end of a reaction cycle or extend the reaction cycle, if no regeneration can be performed at a particular time for operational reasons. Examples can be the missing operability of a parallel reactor, for example because of a re-

placement of the catalyst in the latter, as well as a lack of availability of operating materials for an upcoming regeneration. For this purpose, a switch is made from a uniform distribution of the educt mixture partial streams to the changed supply of feed according to claim 1.

Preferred Aspects of the Invention

Preferably, the process according to the invention is carried out such that the reduced educt mixture partial stream is not more than 70 %, preferably not more than 50 % of the next larger educt mixture partial stream. As compared to a lower reduction, larger effects and advantages in terms of the extension of a reaction cycle are obtained in this way.

A particularly distinct extension of the reaction cycle is observed when in the process according to the invention the educt mixture partial stream supplied to the last reaction zone of the olefin synthesis reactor in flow direction not only is reduced, but decreased to zero. In addition, an educt mixture partial stream reduced for example to 50 % or more optionally can be supplied to a reaction zone arranged further upstream.

In a preferred aspect of the process according to the invention, at least one recirculation stream additionally is supplied to the first and/or at least one succeeding reaction zone, which is obtained in the further processing of the reactor product. Water for example can serve as recirculation stream, which has been obtained from the product stream of the olefin synthesis reactor by condensation and optionally has been subjected to an aftertreatment. Furthermore, hydrocarbon streams, which are obtained in the course of the processing of the reactor product of the olefin synthesis reactor, also can partly be recirculated to the latter. As a result, the components contained therein, such as for example higher olefins like butenes, pentenes, hexenes, heptenes or octenes, additionally can be converted to ethylene and propylene, whereby the yield rises for these target products. In all cases, the temperature control of the olefin synthesis reactor is improved by charging the same with recirculation streams.

In a particularly preferred aspect, the olefin synthesis reactor contains six reaction zones; thus, a first and five succeeding reaction zones are provided. Sufficient operating

experience already exists with this reactor construction (see the document WO 2007/140844 A1 discussed above), so that the process according to the invention can be applied particularly easily and its advantages as compared to the operation with uniformly distributed supply of the educt mixture partial streams can be recognized particularly clearly. This is the case in particular when no educt mixture partial stream is supplied to the sixth reaction zone in flow direction, but the same only is charged with the product stream of the upstream catalyst zone.

An advantageous aspect of the process according to the invention provides that an educt mixture partial stream added to a succeeding reaction zone is reduced from an initial value to a final value, with the reduced fraction being distributed to the other educt mixture partial streams, whereby the mass flow of the educt mixture supplied to the reactor remains constant overall. Due to the increased methanol conversion with constant selectivity to the target products, the yield of these target products thus can be increased further beside the extension of the reaction cycle.

In an alternative aspect of the process according to the invention it is provided that an educt mixture partial stream added to a succeeding reaction zone is reduced from an initial value to a final value, without the reduced fraction being distributed to the other educt mixture partial streams, whereby the mass flow of the educt mixture supplied to the reactor overall is reduced by this reduced fraction. This aspect for example can be utilized when switching from the synthesis operation into the regeneration mode. In this case, when the load of the upstream reaction zones is not changed, but the educt mixture partial stream, which is added to the succeeding reaction zone or zones, is reduced, a reduced total feed quantity of the educt mixture supplied to the reactor is obtained, which results in a lower propylene production, but a higher propylene yield relative to the feed quantity.

It was found to be particularly favorable that the conversion in the olefin synthesis reactor is carried out at temperatures of 300 to 600 °C, preferably at temperatures of 360 to 550 °C, most preferably at temperatures of 400 to 500 °C, and at pressures of 0.1 to 20 bar, absolute, preferably at pressures of 0.5 to 5 bar, absolute, most preferably at pres-

sures of 1 to 3 bar, absolute. The previous studies have shown that under these operating conditions particular advantages are obtained with regard to the yield of target products as well as the duration of the reaction cycles.

In principle, the invention can be utilized with all types of catalyst which are active for the conversion of oxygenates to olefins. Particular advantages are obtained, however, when the reaction zones contain a granular, form-selective zeolite catalyst of the pentasil type, preferably ZSM-5, in the form of a fixed bed. Suitable catalysts of this type are commercially available.

Exemplary embodiments and numerical examples

Further developments, advantages and possible applications of the invention can also be taken from the following description of exemplary embodiments and numerical examples and the drawings. All features described and/or illustrated form the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

In the only Figure

Fig. 1 shows a schematic representation of an olefin synthesis reactor with six reaction zones in a longitudinal section as well as the position of the inlets of the educt mixture partial streams.

In the olefin synthesis reactor 1 schematically shown in Fig. 1 a total of six reaction zones 2a to 2f are provided, which contain a bed of granular, commercially available catalyst. The catalyst is a ZSM-5-based zeolite active for the conversion of oxygenates such as methanol and DME to short-chain olefins, which can be obtained for example from Süd-Chemie AG under the designation MTPROP®. Details of the arrangement of the catalyst in the reactor and of the operation of the reactor can be found in the document WO 2007/140844 A1 already mentioned above. The suitable conversion conditions of said oxygenates to short-chain olefins also are mentioned in the last-mentioned WO publication; they are also known in principle to the skilled person and can be determined for the specific reaction conditions and the catalyst used by means of routine ex-

periments. In doing so, care should be taken that a rather complete methanol conversion is achieved at a catalyst temperature which is not too high. In this way, an optimum result is obtained with regard to high methanol conversions, high yields of short-chain olefins and a long catalyst life.

In the embodiment shown in Fig. 1, the catalyst volume per reaction zone increases in flow direction, in order to achieve an approximately constant value for the space velocity in each reaction zone, since the volumetric gas flow is increased by supplying the educt mixture partial streams step by step.

In the present exemplary embodiment, the educt mixture is divided into six partial streams, which are supplied to the individual reaction zones via conduits 3a to 3f. Via flow controllers for each supply conduit 3a to 3f, which are only indicated, but not shown in detail in Fig. 1, the division is effected such that the reaction zones are charged with educt mixture mass flows of equal size. The educt mixture partial stream is supplied to the first reaction zone via conduit 3a. The first reaction zone additionally is charged with a steam stream via conduit 5 and with one or more recirculation streams containing hydrocarbons via conduit 6. Before entry into the catalyst bed of the first reaction zone, all partial streams supplied are intermixed with suitable measures known to the skilled person.

The second reaction zone 2b, as well as the succeeding reaction zones 2c to 2f, each are charged with an educt mixture partial stream and in addition with the product stream leaving the upstream reaction zone; this is indicated in Fig. 1 by vertical flow arrows after the respective reaction zone. The supply of the educt mixture partial stream is effected via suitable distributor systems described in detail in WO 2007/140844 A1, in order to achieve a homogeneous distribution of the educt mixture over the reactor cross-section.

According to the invention, the last reaction zone 2f in flow direction is charged with an educt mixture partial stream via conduit 3f, whose mass flow is reduced distinctly, preferably by at least 50 %, as compared to the educt mixture partial streams supplied upstream via conduits 3a to 3e. According to a particularly preferred aspect of the inven-

tion, the educt mixture partial stream in conduit 3f is zero, i.e. no fresh educt mixture is supplied to the reaction zone 2f. In this embodiment, the reaction zone 2f therefore serves as pure post-reaction zone.

Via conduit 4, the product mixture leaves the olefin synthesis reactor 1 and is supplied to the product processing known per se, which is described for example in the European Patent Application EP 0448000 A1 and the European Patent Specification EP 1289912 B1.

Numerical Examples

The following results were obtained in tests in a pilot plant, comprising an olefin synthesis reactor with six reaction zones according to Fig. 1. Under standard operating conditions, a total methanol mass flow of 1050 g/h was supplied to the reactor, wherein each individual catalyst bed (six catalyst beds in all) was loaded with a space velocity (WHSV) related to the catalyst mass of 0.7 h^{-1}. In addition, the reactor was charged with a constant steam mass flow of 1000 g/h. The inlet temperature into the first catalyst bed of the olefin synthesis reactor was between 460 and 470 °C and the outlet temperature for all beds was about 480 °C. The pressure at the reactor outlet was 1.3 bara. The catalyst quantity per catalyst bed was different, with the first catalyst bed having the smallest catalyst quantity and the catalyst quantity rising step by step in the downstream beds. The sixth and last catalyst bed accordingly contained the highest catalyst quantity. Consequently, the quantity of the educt mixture added to the individual catalyst beds also was rising. The test results obtained thereby are listed in the following Table.

During test phase 1, standard operating conditions were used (WHSV = 0.7 h^{-1} for each catalyst bed and a total quantity of 1050 g/h of methanol plus 1000 g/h of water). During test phases 2 and 3 on the other hand, the methanol supply to the reaction zone 6 (corresponds to 2f in Fig. 1) was stopped completely, i.e. the last, sixth catalyst bed only was charged with the product stream of the fifth, upstream catalyst bed. At the same time, the space velocity for the other catalyst beds 2a to 2e was uniformly increased from 0.7 h^{-1} to 0.94 h^{-1}, in order to keep the mass flow of 1050 g/h of methanol to the entire reactor constant. Finally, during test phase 3 the space velocity for all catalyst

beds, except for the last, again was reduced to 0.7 h^{-1}, wherein the last catalyst bed in turn only was charged with the product stream of the upstream catalyst stage. This corresponds to a reduction of the methanol mass flow to the reactor from 1050 to 780 g/h.

Test phases 1 to 3 were carried out in the time sequence corresponding to their numbering and without interposition of a catalyst regeneration.

Table: Conversion of methanol to propylene in a six-stage olefin synthesis reactor with distributed addition of the methanol feed

Test phase	Total feed of MeOH	MeOH to Rct.zone 6	Total run time	Methanol conversion	Propylene yield[#)]	Propylene production
	g/h	g/h	**h-o-s**	X(MeOH) to HC	**wt-%**	**g/h**
1	1050	268.8	**23**	94.8%	27.6	274.5
1	1050	268.8	**35**	94.3%	27.3	270.5
1	1050	268.8	**47**	94.0%	27.2	268.2
1	1050	268.8	**59**	92.9%	27.2	264.6
1	1050	268.8	**71**	92.3%	27.2	263.8
1	1050	268.8	**83**	91.3%	27.4	264.1
1	1050	268.8	**95**	90.6%	27.4	263.2
Mean value				***92.9%***	***27.3***	***267.0***
2	1050	0.0	**107**	94.5%	27.4	269.3
2	1050	0.0	**119**	95.4%	27.0	271.5
2	1050	0.0	**131**	94.8%	28.1	279.5
2	1050	0.0	**143**	94.6%	29.0	288.8
2	1050	0.0	**155**	93.7%	28.6	281.9
2	1050	0.0	**167**	93.9%	27.9	276.5
2	1050	0.0	**179**	93.4%	28.4	279.6
2	1050	0.0	**191**	93.1%	28.6	282.4
Mean value				***94.2%***	***28.1***	***278.7***
3	780	0.0	**215**	94.5%	30.9	228.1
3	780	0.0	**227**	93.9%	29.6	217.8
3	780	0.0	**239**	93.7%	29.0	213.2
3	780	0.0	**251**	93.2%	29.8	217.9
3	780	0.0	**263**	93.0%	30.3	221.6
3	780	0.0	**275**	92.7%	30.2	220.2
3	780	0.0	**287**	92.6%	30.2	219.8
Mean value				***93.4%***	***30.0***	***219.8***

[#)] Definition: g/h propylene / (g/h MeOH, in - (g/h MeOH, out + g/h DME, out))

With reference to the data shown in the Table it can be seen that switching from a uniform distribution of the methanol feed over all six reaction zones (test phase 1) to an

operation in which only the first five reaction zones in flow direction (Figs. 1, 2a to 2e) are charged with fresh methanol feed, and to the sixth reaction zone (Figs. 1, 2f) merely the product stream leaving the fifth reaction zone (2e) is supplied (test phase 2), leads to a significant increase of the methanol conversion to hydrocarbon products and the propylene yield and hence also to the propylene production. In practice, this means that in operation by the process according to the invention the olefin synthesis reactor can be operated longer as compared to the operating conditions corresponding to test phase 1, until an admissible minimum methanol conversion is fallen short of and therefore a regeneration must be carried out.

When reducing the total methanol feed from 1050 to 780 g/h in test phase 3, a further increase of the propylene yield can be observed. But since less methanol is converted overall, the propylene production decreases distinctly. However, the propylene yield now is increased distinctly and roughly amounts to 30 wt-% as compared to 27.3 wt-% in test phase 1 and 28.1 wt-% in test phase 2. The test conditions during test phase 2, which correspond to a particularly preferred aspect of the process according to the invention, therefore represent an optimum with regard to a high propylene production with a prolonged cycle time at the same time.

Industrial Applicability

With the invention, a process for producing short-chain olefins is proposed, which is characterized by a high yield of ethylene and in particular propylene with an extension of the cycle time at the same time and thus a reduced number of regenerations per catalyst charge. The application of the process according to the invention increases the flexibility with regard to the choice of the time for the regeneration operation.

List of Reference Numerals

[1]	olefin synthesis reactor
[2a-2f]	reaction zone
[3a-3f]	conduit educt mixture partial stream
[4]	conduit product
[5]	conduit steam
[6]	conduit recirculation stream

Claims

1. A process for producing a hydrocarbon product containing olefins, comprising ethylene and propylene, by converting an educt mixture comprising steam and oxygenates, such as methanol and/or dimethyl ether, which is divided into several partial streams, to olefins under oxygenate conversion conditions in a reactor with a plurality of series-connected reaction zones which are in fluid connection with each other, comprising a first reaction zone and at least one succeeding reaction zone, wherein the first reaction zone is charged with an educt mixture partial stream and steam as well as optionally recirculation streams, and the succeeding reaction zones are charged with an educt mixture partial stream and the succeeding reaction zones additionally are charged with the product stream of the upstream reaction zone,
characterized in that
at least one of the succeeding reaction zones is charged with a reduced educt mixture partial stream which is smaller than the educt mixture partial stream supplied to the upstream reaction zone.

2. The process according to claim 1,
characterized in that
the reduced educt mixture partial stream is not more than 70 %, preferably not more than 50 % of the next larger educt mixture partial stream.

3. The process according to claim 1,
characterized in that
the reduced educt mixture partial stream is zero.

4. The process according to claims 1 to 3,
characterized in that
the reduced educt mixture partial stream is supplied to the last reaction zone in flow direction.

5. The process according to any of the preceding claims,
characterized in that
at least one recirculation stream additionally is supplied to the first and/or at least one succeeding reaction zone, which is obtained in the further processing of the reactor product.

6. The process according to claims 1 to 5,
characterized in that
a first and five succeeding reaction zones are provided.

7. The process according to claim 6,
characterized in that
the reduced educt mixture partial stream is supplied to the sixth reaction zone in flow direction and that the reduced educt mixture partial stream is zero.

8. The process according to any of the preceding claims,
characterized in that
an educt mixture partial stream added to a succeeding reaction zone is reduced from an initial value to a final value, with the reduced fraction being distributed to the other educt mixture partial streams, whereby the mass flow of the educt mixture supplied to the reactor remains constant overall.

9. The process according to any of the preceding claims,
characterized in that
an educt mixture partial stream added to a succeeding reaction zone is reduced from an initial value to a final value, without the reduced fraction being distributed to the other educt mixture partial streams, whereby the mass flow of the educt mixture supplied to the reactor overall is reduced by this reduced fraction.

10. The process according to any of the preceding claims,
characterized in that

the conversion is carried out at temperatures of 300 to 600 °C, preferably at temperatures of 360 to 550 °C, most preferably at temperatures of 400 to 500 °C.

11. The process according to any of the preceding claims,
characterized in that
the conversion is carried out at pressures of 0.1 to 20 bar, absolute, preferably at pressures of 0.5 to 5 bar, absolute, most preferably at pressures of 1 to 3 bar, absolute.

12. The process according to any of the preceding claims,
characterized in that
the reaction zones contain a granular, form-selective zeolite catalyst of the pentasil type, preferably ZSM-5, in the form of a fixed bed.

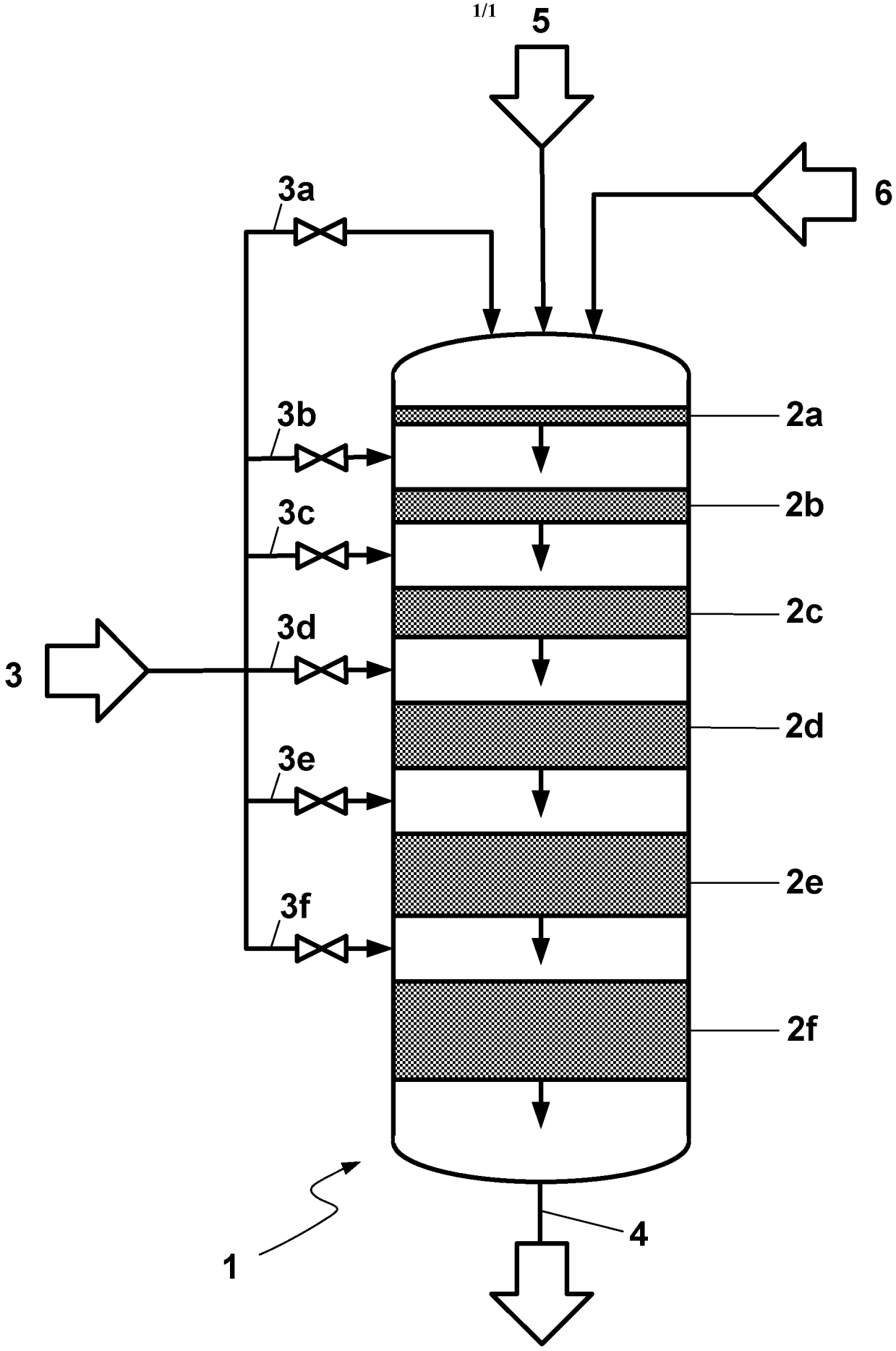

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/059336

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/04 C07C1/20
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2007/140844 A1 (LURGI AG [DE]; BACH HERMANN [DE]; BREHM LOTHAR [DE]; BOHLE JUERGEN [DE) 13 December 2007 (2007-12-13) cited in the application the whole document -----	1-12
Y	WO 01/92190 A1 (MG TECHNOLOGIES AG [DE]; HACK MARKUS [DE]; KOSS ULRICH [DE]; KOENIG PE) 6 December 2001 (2001-12-06) the whole document -----	1-12
Y	US 4 404 414 A (PENICK JOE E [US] ET AL) 13 September 1983 (1983-09-13) column 6, lines 41-56; figures column 6, line 67 - column 7, line 11 column 8, line 8 column 8, line 59 - column 9, line 18 column 10, lines 22-30; claims; examples -----	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 August 2013	29/08/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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