

Process and Apparatus for Producing Dimethyl Ether from Methanol

This invention relates to a process and an apparatus for producing dimethyl ether (DME) from methanol (MeOH) by converting, preferably by acid-catalytic condensation, raw MeOH obtained through MeOH synthesis to DME by splitting off water in a reactor, in which the feed mixture consisting of raw MeOH and a process-internally obtained return flow substantially formed from unconverted MeOH and reaction water are charged to a column, subsequently referred to as MeOH column, and evaporated, and the distillate substantially consisting of vaporous MeOH is supplied to the reactor.

Nowadays, MeOH exclusively is produced from the synthesis gases CO_2/H_2 or CO/H_2 , which in turn originate from the reforming of natural gas, residue oils of crude oil processing or from the pressure gasification of coal. The raw MeOH produced can directly be processed to DME or be processed by distillation to obtain pure MeOH and subsequently be catalytically converted to DME and water. In both cases, the DME product obtained is separated from unconverted MeOH and water by distillation. In general, the raw MeOH is subjected to a two- or three-stage distillation, in which first the low boilers and the dissolved gases, in particular CO_2 , are removed and then MeOH and water are separated, and in an adiabatic fixed-bed reactor the purified MeOH is converted to DME up to the reaction equilibrium. Since the reactor product consists of a mixture of DME, water, unconverted MeOH and minor amounts of uncondensable light gases, the reactor product is treated in a two-stage distillation, wherein in the head of the first distillation stage DME is separated from unconverted MeOH and reaction water and in the head of the second distillation stage the MeOH contained in the bottom product of the first stage is separated from the reaction water and the MeOH obtained flows back into the reactor. The uncondensable light gases discharged with the DME at the top of the first distillation stage are saturated with DME which in a gas washing stage is separated from the uncondensable gases by using MeOH as washing agent, before the same leave the

system as low boilers at the top of the gas washing stage. Accordingly, both in the distillation of DME and in the distillation of MeOH mixtures chiefly consisting of MeOH, water and DME are separated. Since the product specifications for DME on the one hand and MeOH on the other hand must satisfy various requirements, the distillations of DME and MeOH are carried out separately. The above-described measures are applied in particular for the production of high-purity DME, which is widely used as propellant gas, e.g. in hair spray and paint spray. Technical DME is an alternative to liquefied gases with excellent burning properties. Due to a cetane number of 55 to 60, DME can be used in diesel engines as a substitute for diesel fuel.

Since according to the Biofuels Directive 2003/30/EG of the European Parliament and the "Council for Promoting the Use of Biofuels or other Renewable Fuels in the Transport Sector" DME is regarded as biofuel, the same may contain impurities which are not allowed for high-purity DME. Therefore, the distillation of the MeOH can be omitted and the raw MeOH can directly be charged to the DME reactor. In the process described in US 5,750,799 A, for example, untreated raw MeOH is directly introduced into a DME reactor, so that the return flow containing the MeOH is loaded with considerable amounts of water. This circulating water must be condensed in addition to the unconverted MeOH and must subsequently be evaporated before the DME reactor, whereby the energy efficiency of the process is impaired considerably. In addition, the circulating stream is increased due to the reduced MeOH conversion in the DME reactor and accordingly the apparatuses and technical components of the plant for producing DME must be designed larger. Raw MeOH contains carbonic acid H_2CO_3 and small amounts of organic acids which must be neutralized, in order to avoid corrosion phenomena on apparatuses and technical components made of steel, which are used for producing DME. Usually soda is used for neutralizing the raw MeOH.

US 6,740,783 B1 describes a process for producing DME from raw MeOH by using a DME reactor with a fixed bed of zeolite catalyst which initially is deactivated by doping with metals, in order to increase the DME selectivity of the catalyst. On the long run, however, a constant supply of metals leads to a continuous deactivation and hence to a reduction of the useful life of the catalyst. The subject-matter of EP 1396483 B1 is a process for producing DME, in which raw MeOH is dehydrated in the vapor phase in the presence of an activated Al_2O_3 catalyst doped with Na. A limited doping with Na is

important, so as not to impair the conversion of the catalyst. This means that the raw MeOH must be largely free from metal and NH_4 ions. In the provided raw MeOH and its evaporation the entrainment of neutralizing agent must therefore be carefully avoided.

In the documents CN 100366597 C, CN 1830934 A and JP 2004161673 A apparatuses are described, in which raw MeOH and reflux MeOH are supplied to a common separating means. The reflux MeOH contains the entire reaction water originating from the DME reactor, so that the reflux MeOH cannot be charged to the top of the distillation column. Therefore, the use of an overhead condenser is provided, in order to lower the water content of the raw MeOH supplied to the DME reactor. This requires a considerable condenser capacity which involves a correspondingly greater performance of the reboiler, whereby the energy efficiency and the economy are reduced. JP 2004161672 A deals with an evaporator for raw MeOH, which allows a partial evaporation of the raw MeOH, wherein the non-evaporated mixture of MeOH and water together with the unconverted MeOH and the reaction water from the DME reactor is separated into process water and reflux MeOH in a separate distillation column operating at low pressure. The subcooled water-poor liquid reflux MeOH is contacted with the evaporated raw MeOH, so that the water concentration in the raw MeOH supplied to the DME reactor is lowered. Hence, it is provided to also pass non-evaporated MeOH to the reflux MeOH column along with the non-evaporated water of the raw MeOH. This measure requires the evaporation and condensation of the MeOH in the reflux MeOH column and after the return of the largely water-free MeOH to the raw MeOH evaporator the renewed evaporation of the same MeOH. Thus, a MeOH circuit without contact with the DME reactor is obtained, which consumes unnecessary energy and reduces the efficiency of the circuit.

From EP 455004 A1 or US 5,750,799 A it is known to wash out in a column the DME discharged with the uncondensable gases at the head of the DME column and recirculate the same to the MeOH column. This measure leads to a DME content in the raw MeOH charged to the DME reactor, by which the conversion of MeOH to DME is reduced. This is relevant in particular when raw MeOH is used and the light gases contained in the raw MeOH are not separated before the DME reactor, but only in the DME column. Proportional to the amount of the non-condensed light gases, the amount of the DME discharged with the gases and hence the amount of DME in the inflow to the DME reactor increases.

When the raw MeOH contains only little dissolved gases, the arrangement of a scrubber can be omitted. Instead, the DME discharged with the uncondensable gases can largely be recovered in an end cooler operated with cold water or a refrigerant.

The object underlying the invention consists in designing the process described above such that a rather low consumption of operating resources is achieved, the installed heat transfer capacity is improved and the useful life of the catalyst is not impaired.

This object is solved in that in a column, subsequently referred to as mixture column, the reaction mixture withdrawn from the reactor is separated into a bottom product chiefly consisting of water and into a distillate chiefly formed from DME and MeOH, in a column, subsequently referred to as DME column, the distillate is separated into a distillate substantially containing DME and uncondensable gases to be released overhead and into a bottom product formed from water-poor MeOH, which is supplied to the top of the MeOH column.

The term "distillate" defines the product withdrawn in a distillation or rectification column as side product or as top product.

In accordance with the aspect of the invention, the bottom product of the DME column, which is formed from water-poor MeOH, is supplied to the top of the MeOH column or mixed with the bottom product withdrawn from the forerun column.

In accordance with another feature of the invention it is possible to cool or partly condense the reaction mixture withdrawn from the reactor in a process-internal heat exchanger, before the reaction mixture is charged to the mixture column.

The amount of water of the distillate of the mixture column, which is introduced into the DME column and chiefly consists of DME and MeOH, is adjustable via the reflux ratio of the amount of liquid produced at the top of the column by condensation of a part of the top product and charged again at the top of the column and the amount of top product discharged to the DME column. By means of this measure, the quality of the water-poor liquid reflux MeOH withdrawn from the bottom of the DME column can be optimized.

Another feature of the invention can be seen in that a part of the vapor produced by evaporating the return flow of the bottom product of the MeOH column substantially consisting of water is introduced into the bottom of the mixture column and in this way the DME content in the bottom is decreased.

One aspect of the invention furthermore can be seen in that the distillate of the DME column substantially consisting of DME is condensed and one part of the condensate is charged as return flow to the top of the DME column and the other part of the DME condensate is discharged. Due to the fact that at the same time the bottom product of the DME column consisting of water-poor liquid MeOH is charged to the top of the MeOH column, the condensation in the MeOH column can be omitted.

It is also possible that the DME condensed in the DME column is discharged from the fortification section of the DME column as side product.

Another feature of the invention can be seen in that the DME discharged with the uncondensable gases is washed out in a washing column, preferably with MeOH, and passed into the mixture column.

In accordance with the additional aspect of the invention, the gases and low-boiling components dissolved in the inflowing raw MeOH are separated from the inflowing raw MeOH before evaporation of the MeOH in the MeOH column and the distillate is discharged, whereby the quality of the DME produced is improved and the amount of DME entrained from the DME column with the uncondensable gases is reduced.

The bottom product withdrawn from the forerun column is preheated and/or partly evaporated before flowing into the MeOH column.

One aspect of the process of the invention furthermore consists in that the DME discharged with the uncondensable gases at the top of the DME column is washed out in a washing column, preferably with MeOH, and the bottom product produced is passed into the DME column and/or added to the raw MeOH prior to entry into the MeOH column.

In accordance with another feature of the invention, raw MeOH branched off from the inflow of the raw MeOH can be charged to the top of the washing column as washing agent.

When the raw methanol contains only small amounts of dissolved gases, the arrangement of a washing column can be omitted and instead an end cooler operated with cold water or refrigerant, for example DME, can be used, with which the DME discharged with the uncondensable gases can be recovered.

It is expedient to combine the distillate of the forerun column, which contains dissolved gases and low-boiling components, with the distillate of the washing column, which contains uncondensable gases, and to discharge the mixture for further processing.

In accordance with an additional feature of the invention, the bottom product of the MeOH column, which chiefly consists of water, is discharged from the process or supplied to the lower part of the mixture column and then discharged via the bottom of the mixture column.

It is also possible that the bottom product of the mixture column, which chiefly consists of water, is passed into the MeOH column and the water is discharged from the process via the bottom of the MeOH column.

It is advantageous that before introduction into the reactor the distillate of the MeOH column, which contains MeOH, is superheated to a reaction temperature of 250 to 330°C by indirect heat transfer from the reaction heat contained in the reaction mixture discharged from the reactor.

A part of the gaseous distillate of the MeOH column is passed into the bottom of the DME column.

In the apparatus for carrying out the process the DME column is arranged on the MeOH column in accordance with the invention. The two columns are coupled via the distillate of the MeOH column and the bottom product of the DME column, so that the MeOH column

can be operated without reflux cooler and the DME column can be operated without evaporator.

A modification of the process of the invention consists in that the vaporous distillate of the mixture column, which chiefly consists of DME and MeOH, is fed into the bottom of a rectification column, subsequently referred to as DME product column, the bottom product of this column, which contains liquid MeOH, is charged to the top of a rectification column, subsequently referred to as MeOH reflux column, wherein the distillate thereof is passed into the bottom of the DME product column and the bottom product thereof is supplied to the top of the MeOH column.

In the inventive modification of the process the DME product column formed as fortification section is arranged on the mixture column and the MeOH reflux column formed as stripping section is arranged on the MeOH column. By means of this measure, the fortification section and the stripping section of the DME column virtually are separated and the smaller stripping section of the DME column can be put onto the methanol column and the larger fortification section of the DME column can be put onto the mixture column. The diameters of the mixing column and of the fortification section of the DME column are almost the same.

Further features, advantages and possible applications of the process of the invention can also be taken from the following description of an embodiment and from the apparative process flow diagrams illustrated in the drawing in Fig. 1 and Fig. 2. All features described and/or illustrated form the subject-matter of the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

According to Fig. 1, a feed stream consisting of raw MeOH with an MeOH content of 75 wt-% is fed via conduit (1) into the forerun column (2) in which at a mean temperature of 80°C and a mean pressure of 3 bar[a] the gases dissolved in the raw MeOH, such as CO, CO₂, CH₄, and the low-boiling hydrocarbons are discharged via conduit (3) for further utilization. The MeOH withdrawn with a mean temperature of 100°C from the bottom of the forerun column (2) via conduit (4) is preheated to a mean temperature of 160°C in a heat exchanger group (5), partly evaporated thereby and charged via conduit (6) to a MeOH column (7) in which the water is separated from the MeOH at a mean temperature

of 180°C and a mean pressure of 20 bar[a]. From the bottom of the MeOH column (7) the water is discharged from the process via conduit (8), while the gaseous top product of the MeOH column, which is discharged via conduit (7) with a mean temperature of 170°C, is heated to a mean temperature of 300°C in a heat exchanger group (10) and passed into a reactor (12) via conduit (11). The gas mixture withdrawn at the bottom of the reactor (12) is supplied to the heat exchanger group (10) via conduit (13) and cooled recuperatively, before it is charged to the mixture column (15) via conduit (14). In the mixture column (15) the gas mixture is separated into a water-rich bottom product and a water-poor top product at a mean pressure of 15 bar[a] and a mean temperature of 150°C, wherein the top product contains less than 5 wt-%, preferably less than 2 wt-% of water. The water-rich bottom product is passed to the MeOH column (7) via conduit (16). The water-poor top product is supplied via conduit (17) to the DME column (18) which operates at a mean temperature of 100°C and a pressure of 13.5 bar[a]. From the top of the DME column (18) or from the side, two to seven trays below the overhead condenser, DME is withdrawn and passed to the plant boundary via conduit (19). The bottom product of the DME column (18), which chiefly consists of MeOH with small amounts of water, is pumped to the top of the MeOH column (7) via conduit (20) and serves as return flow for the fortification section of the MeOH column (7). To keep the concentration of DME in the bottom of the DME column (18) as low as possible, a partial stream of the top product of the MeOH column (7) flowing in conduit (9) can be branched off and be introduced into the bottom of the DME column (18) via conduit (21), so that in this case an evaporator circuit can be omitted.

The gases not condensable in the DME column (18) are withdrawn overhead and passed via conduit (22) into the bottom of the washing stage (23) in which the DME contained in the uncondensable gases is recovered at a mean pressure of 10 bar[a] and a mean temperature of 75°C along with the MeOH branched off from conduit (4) and charged to the top of the washing stage (23) via conduit (24). Via conduit (25) the gaseous top product of the washing stage (23) is combined with the top product of the forerun column (2) flowing off via conduit (3) and discharged for further utilization. Via conduit (26) the washing agent containing DME is pumped from the bottom of the washing stage (23) into the mixture column (15). Alternatively, the bottom product of the washing stage (23) can either be fed into the DME column (18) via conduit (27) or be fed via conduit (28) into the

MeOH stream flowing to the MeOH column (7) in conduit (6). The mixture column (15) can be operated without evaporator circuit.

In the modification of the process flow diagram according to Fig. 1, which is represented in Fig. 2, the water-poor product discharged from the top of the mixture column (15) via conduit (17) is directly passed into the bottom of a rectification column (30), subsequently referred to as DME product column, which is formed as fortification column mounted on the mixture column (15). The bottom product of the DME product column (30), which chiefly consists of MeOH with small amounts of water, is supplied via conduit (31) to the top of a column (32), subsequently referred to as MeOH reflux column, which is formed as stripping column and arranged on the MeOH column (7). Via conduit (20) the bottom product of the MeOH reflux column (32) flows to the top of the MeOH column (7), while the top product is passed into the bottom of the DME product column (30) via conduit (33). The partial stream branched off from the top product of the MeOH column (7) flowing in conduit (9) is supplied to the bottom of the MeOH reflux column (32) via conduit (21).

The advantages achieved with the invention can be seen in particular in a comparatively improved energy efficiency and economy. A comparison of the process of the invention with a known process belonging to the prior art, as described for example in JP 2004161672 A, shows that under the same marginal conditions for the MeOH content of the raw MeOH, the preheating and partial evaporation of the MeOH prior to entry into the MeOH column, the inlet temperature into the reactor, the purity of the DME produced and the purity of the process water obtained, and with almost the same external energy consumption, the totally installed heat exchanger performance is smaller than in the known process by about 20 %.

Claims:

1. A process for producing dimethyl ether (DME) from methanol (MeOH) by converting, preferably by acid-catalytic condensation, raw MeOH obtained through MeOH synthesis to DME by splitting off water in a reactor (12), in which the feed mixture consisting of raw MeOH and a process-internally obtained return flow substantially formed from unconverted MeOH and reaction water, are charged to a MeOH column (7) and evaporated, and the distillate substantially consisting of vaporous MeOH is supplied to the reactor, **characterized in that** in a mixture column (15) the reaction mixture withdrawn from the reactor (12) is separated into a bottom product chiefly consisting of water and into a distillate chiefly formed from DME and MeOH, in a DME column (18) the distillate is separated into a distillate substantially containing DME and uncondensable gases discharged overhead and into a bottom product formed from water-poor MeOH, which is supplied to the top of the MeOH column (7) or mixed with the bottom product withdrawn from the forerun column (2).
2. The process according to claim 1, **characterized in that** the reaction mixture withdrawn from the reactor (12) is cooled in a process-internal heat exchanger (10) or partially condensed, before it is charged to the mixture column (15).
3. The process according to any of claims 1 and 2, **characterized in that** the amount of water of the distillate of the mixture column (15) supplied to the DME column (18), which chiefly consists of DME and MeOH, is adjustable via the reflux ratio of the amount of liquid produced at the top of the column by condensation of a part of the top product and charged again to the top of the column and the amount of top product discharged to the DME column.
4. The process according to any of claims 1 to 3, **characterized in that** a part of the vapor produced by evaporating the return flow of the bottom product of the MeOH column (7), which substantially consists of water, is passed into the bottom of the mixture column (15).
5. The process according to any of claims 1 to 4, **characterized in that** the distillate of the DME column (18) substantially consisting of DME is condensed and one part of

the condensate is charged to the top of the DME column as return flow and the other part is discharged.

6. The process according to any of claims 1 to 5, **characterized in that** the DME condensed in the DME column (18) is discharged from the ascending section of the DME column as side product.
7. The process according to any of claims 1 to 6, **characterized in that** the DME discharged from the DME column (18) with the uncondensable gases is washed out in a washing column (23), preferably with MeOH, and passed into the mixture column (15).
8. The process according to any of claims 1 to 7, **characterized in that** before evaporation of the MeOH in the MeOH column (7) the gases and low-boiling components dissolved in the raw MeOH are separated from the inflow of raw MeOH to be separated in a forerun column (2), and the distillate is discharged from the process.
9. The process according to any of claims 1 to 8, **characterized in that** the inflow of raw MeOH to be separated is preheated and/or partly evaporated before the MeOH column (7).
10. The process according to any of claims 1 to 9, **characterized in that** the DME discharged from the DME column (18) with the uncondensable gases is washed out in a washing column (23), preferably with MeOH, and the bottom product produced is passed into the DME column (18) and/or added to the raw MeOH prior to entry into the MeOH column (7).
11. The process according to any of claims 1 to 10, **characterized in that** raw MeOH branched off from the inflow of MeOH as washing agent is charged at the top of the washing column (23) or a partial stream of the bottom product of the DME column (18) is used.

12. The process according to any of claims 1 to 11, **characterized in that** the distillate of the forerun column (2), which contains dissolved gases and low-boiling components, is combined with the top product of the washing column (23) which contains uncondensable gases.
13. The process according to any of claims 1 to 12, **characterized in that** the bottom product of the MeOH column (7), which chiefly consists of water, is passed into the lower part of the mixture column or discharged from the process.
14. The process according to any of claims 1 to 13, **characterized in that** the bottom product of the mixture column (15), which chiefly consists of water, is passed into the MeOH column (7) or discharged from the process.
15. The process according to any of claims 1 and 14, **characterized in that** before introduction into the reactor (12) the distillate of the MeOH column (7), which contains MeOH, is superheated to a reaction temperature of 250 to 330°C by indirect heat transfer from the reaction heat contained in the reaction mixture discharged from the reactor.
16. The process according to any of claims 1 to 15, **characterized in that** a part of the distillate of the MeOH column (7) is passed into the bottom of the DME column (18).
17. Modification of the process according to any of claims 1 to 16, **characterized in that** the vaporous distillate of the mixture column (15), which chiefly consists of DME and MeOH, is fed into the bottom of a DME product column (30), the bottom product of the DME product column, which contains liquid MeOH, is charged to the top of an MeOH reflux column (32), whose distillate is passed into the bottom of the DME product column (30) and whose bottom product is charged to the top of the MeOH column (7) or added to the bottom product withdrawn from the forerun column (2).
18. An apparatus for performing the process according to any of claims 1 to 17, **characterized in that** the DME column (18) is arranged on the MeOH column (7).

19. An apparatus for carrying out the modification of the process according to any of claims 1 to 18, **characterized in that** the DME product column (30) is formed as fortification column and arranged on the mixture column (15) and the MeOH reflux column (32) is formed as stripping column and arranged on the MeOH column (7).