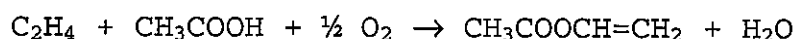


Method for producing vinyl acetate monomer

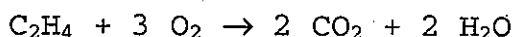
The invention relates to a process for preparing vinyl acetate monomer in a heterogeneously catalysed, continuous gas phase process by reacting ethylene with acetic acid and oxygen in a reactor, wherein the workup of the product stream obtained is energetically optimized.

Vinyl acetate monomer is prepared in continuous processes with recycling of the purified product stream (cycle gas system). In a heterogeneously catalysed gas phase process, ethylene reacts with acetic acid and oxygen over fixed bed catalysts which generally comprise palladium salts and alkali metal salts on a support material and may additionally also be doped with gold, rhodium or cadmium.

The ethylene, oxygen and acetic acid reactants are converted in an exothermic reaction, generally at a pressure of 1 to 30 bar and a temperature of 130°C to 200°C, in a fixed bed tubular reactor (or else fluidized bed reactor) to vinyl acetate monomer:



In the side reaction, ethylene is oxidized to CO₂:



In the preparation of vinyl acetate monomer, a gas mixture consisting predominantly of ethylene, carbon dioxide, ethane, nitrogen and oxygen is circulated. Upstream of the fixed bed tubular reactor, the gas stream is admixed with the acetic acid, ethylene and oxygen reactants and brought to reaction temperature with steam-operated heat exchangers. The cycle gas is enriched with acetic acid upstream of the fixed bed tubular reactor, typically by means of a steam-operated acetic acid saturator (acetic acid evaporator).

The product gas stream leaving the reactor comprises essentially vinyl acetate monomer, ethylene, acetic

acid, water, oxygen, CO₂, and the inerts: nitrogen, argon, methane and ethane. After the reaction, the vinyl acetate monomer reaction product, unconverted acetic acid, water and further condensable components
5 are condensed out of the cycle gas and sent to workup. Uncondensed vinyl acetate monomer is scrubbed out in an acetic acid-operated scrubber. The condensed vinyl acetate monomer and water products and unconverted acetic acid are separated from one another in
10 different, typically steam-operated distillation processes and the remaining ethylene-containing cycle gas is returned after compression.

A substream of the cycle gas is, before being recycled
15 into the reactor, branched off on the pressure side of the cycle gas compressor, supplied to the CO₂ removal of the CO₂ scrubber (CO₂ absorption/desorption) and, after the CO₂ removal, returned back to the suction side of the compressor. Before the CO₂ removal, this substream
20 is typically freed of vinyl acetate monomer in a column (water scrubber) by means of addition of acetic acid and water. The bottom product of this column, which comprises water, acetic acid and VAM, is separated in the azeotrope column which is heated with process
25 steam.

A problem in the process steps for CO₂ scrubbing is the necessity to return the substream on the suction side owing to the pressure drops which occur in the course
30 of scrubbing, with the disadvantage that the entire substream has to be compressed once again (additional compressor load). The suction-side recycling additionally requires that, after the compression, the already purified substream is supplied again to the
35 unpurified cycle gas stream and partly fed back to the CO₂ scrubbing.

A further disadvantage of the process steps for CO₂ scrubbing practised to date is the energy expenditure to separate the crude vinyl acetate monomer obtained after the scrubbing in the cycle gas scrubber in an azeotrope column.

Against this background, it was an object of the present invention to energetically optimise the workup of the substream branched off for CO₂ scrubbing.

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DE 10 2006 038 689 A1 discloses using the heat content of the steam-saturated CO₂ stream obtained from the carbon dioxide desorber in the CO₂ scrubbing to heat the bottom of the pure vinyl acetate monomer column. A disadvantage is the poor heat transfer when a gaseous heat transfer medium is used. Moreover, the heat content of this CO₂ steam is very low owing to the relatively low proportion of steam.

20 The invention provides a process for preparing vinyl acetate monomer in a heterogeneously catalysed, continuous gas phase process by reacting ethylene with acetic acid and oxygen in a reactor, and

a) separating the product gas stream comprising essentially ethylene, vinyl acetate monomer, acetic acid, water, carbon dioxide and further inert gases, and

b) recycling an ethylene- and CO₂-containing cycle gas stream into the reactor, by

30 c) compressing the cycle gas stream in a cycle gas compressor before recycling into the reactor, and

d) branching off a substream of the cycle gas on the suction side or the pressure side of the cycle gas compressor and feeding it to a CO₂ scrubbing, and

35 e) prior to the CO₂ scrubbing, washing it in a water scrubber,

characterized in that

- f) the substream, after the CO₂ scrubbing, is supplied to the cycle gas via a jet compressor, together with ethylene as the motive medium, on the pressure side of the cycle gas compressor and downstream of the withdrawal of the substream to the CO₂ scrubbing, and/or
- g) the bottom product from the water scrubber is fed directly to the preliminary dewatering column.

The continuous preparation of vinyl acetate monomer is preferably conducted in tubular reactors charged with a fixed bed catalyst. These catalysts are generally supported catalysts doped with noble metals or noble metal salts and promoters, for example bentonite spheres doped with palladium and with gold and potassium salts. The reactor is charged with ethylene, oxygen and acetic acid, and the reaction is performed at a pressure of preferably 8 to 12 bar abs. and a temperature of preferably 130°C to 200°C.

The reaction temperature in the fixed bed tubular reactor of preferably 130°C to 200°C is set by means of evaporative water cooling at a pressure of 1 to 30 bar abs. This forms steam, known as the intrinsic steam, with a temperature of 120°C to 185°C, at a pressure of 1 to 10 bar abs., preferably 2.5 to 5 bar abs. The product gas stream emerging from the reactor comprises essentially vinyl acetate monomer, ethylene, acetic acid, water, oxygen, CO₂, and the inerts: nitrogen, argon, methane and ethane.

In general, the gas mixture leaving the fixed bed tubular reactor is passed into a preliminary dewatering column and the liquid phase obtained at the bottom of the column, principally vinyl acetate monomer, acetic acid, ethyl acetate and water, is fed to the crude vinyl acetate monomer collecting vessel. In the downstream azeotrope column, it is separated into vinyl acetate monomer (VAM) and water as the top product, and

acetic acid as the bottom product. The acetic acid is passed into the acetic acid saturator and thus recycled into the process. The VAM withdrawn as the top product is passed via the dewatering column to the pure vinyl acetate monomer column and separated there into VAM and acetic acid.

The gaseous product mixture withdrawn at the top of the preliminary dewatering column, consisting essentially of ethylene and CO₂, is freed in the cycle gas scrubber from all condensable components. The cycle gas stream withdrawn at the top of the cycle gas scrubber is compressed in the cycle gas compressor to compensate for the considerable pressure drops which occur in the reaction circuit, and recycled into the reactor as cycle gas. The pressure level of the cycle gas is preferably 8 to 12 bar abs. After the removal of the condensable vinyl acetate monomer, acetic acid and water components in the cycle gas scrubber, the cycle gas contains preferably 12 to 18% by volume of CO₂.

A substream of the cycle gas is branched off on the suction side or pressure side, preferably the pressure side, of the cycle gas compressor and fed to the CO₂ removal of the CO₂ scrubbing and, after the CO₂ removal, is returned back to the pressure side of the compressor. The substream withdrawn in the cycle gas compressor makes up about 8 to 12% by volume of the overall cycle gas. Downstream of the branch and upstream of the CO₂ scrubber, the substream withdrawn is scrubbed in a column (water scrubber) with supply of water and acetic acid. The liquid bottom product can be collected in the crude vinyl acetate monomer vessel and separated in the downstream azeotrope column. The gaseous top product of the water scrubber, essentially ethylene and CO₂, is fed to the CO₂ scrubbing.

- The cycle gas substream (top product from the water scrubber) is then conducted into a CO₂ absorption/desorption, preferably operated with aqueous potassium carbonate solution. After the CO₂ scrubbing, the cycle gas substream preferably still contains 2 to 6% by volume of CO₂. The pressure drop after cycle gas scrubbing and CO₂ absorption/desorption is generally 2 to 4 bar.
- 10 The cycle gas substream is recycled into the cycle gas stream downstream of the CO₂ scrubbing, on the pressure side of the cycle gas compressor, and downstream of the withdrawal point of the substream to the CO₂ scrubbing. To compensate for the pressure drop, the cycle gas
- 15 substream is brought by means of ethylene, which is obtained from the refinery with a pressure of 20 to 25 bar abs., to a pressure level of preferably 0.5 to 2 bar above the pressure of the cycle gas, and supplied to the cycle gas stream. The cycle gas stream is
- 20 preferably supplied with the required amount of ethylene via a jet compressor (ejectors, injectors), preferably a suction nozzle. In a preferred embodiment, it is also possible to proceed in such a way that the entire ethylene feed which is supplied to the cycle gas
- 25 upstream of the reactor is supplied via the jet compressor.

- Alternatively to this procedure of recycling the cycle gas substream, or in addition thereto, it is also
- 30 possible to proceed in such a way that the operation of the water scrubber upstream of the CO₂ absorption/desorption is reconfigured in accordance with the invention. The water scrubber is preferably operated at a pressure of 8 to 12 abs. and a
- 35 temperature of preferably 18 to 30°C. The cycle gas substream is freed of VAM in the water scrubber by means of acetic acid and freed of entrained acetic acid by means of water. At the top, the gaseous residual

proportion of the cycle gas substream is withdrawn and conducted to the CO₂ scrubbing.

In the inventive modification, the liquid phase
5 obtained at the bottom of the water scrubber, principally vinyl acetate monomer, acetic acid, ethyl acetate and water, is no longer fed to the crude vinyl acetate monomer collecting vessel and separated in the azeotrope column, but rather applied directly to the
10 preliminary dewatering column. In this case, the bottom product is preferably heated by heat exchange with the gaseous product stream emerging from the reactor. In the preliminary dewatering column, a VAM-water azeotrope is then obtained without using external steam
15 and subsequently separated in a phase separator. The steam saving achievable by this measure for the removal of the water supplied to the water scrubber is at a weight ratio of steam/water of about 2:1. By means of this measure, in an industrial scale plant, at a water
20 flow rate of 300 to 500 kg of water/hour, a steam saving of about 1 to/h in the azeotrope column is achieved.

Figure 1 shows a simplified diagram of the process:
25 ethylene-containing cycle gas was contacted with acetic acid in the acetic acid saturator 1, then oxygen was added and the mixture was fed to the tubular reactor 3 via a steam-heated line 2. The cycle gas mixture leaving the reactor, which comprised essentially
30 ethylene, vinyl acetate monomer, acetic acid, carbon dioxide, oxygen and inerts, was fed via line 4 to the preliminary dewatering column 5. The mixture was separated in the preliminary dewatering column 5, and the bottom product comprising essentially VAM, acetic
35 acid and water was fed via line 8 to the crude vinyl acetate vessel 17, and, after transfer via line 18 into the azeotrope column 19, was separated into a VAM fraction and an acetic acid fraction, which were each

worked up further in process steps which are not shown here.

- The top product of the preliminary dewatering column 5 was withdrawn and freed of gaseous VAM by means of scrubbing with acetic acid in the downstream cycle gas scrubber 6. The gas mixture (cycle gas) consisted, after the cycle gas scrubbing, essentially of ethylene with a CO₂ content amounting to about 12% by volume, and was compressed about 3 bar higher with the cycle gas compressor 7. The majority of the cycle gas was recycled via line 14 into the acetic acid saturator 1. A proportion of about 12% by volume of the cycle gas was branched off from the pressure side of the cycle gas compressor 7 and transferred via line 8 into the water scrubber 9, and treated there with acetic acid and then water to remove residual vinyl acetate monomer. The bottom product comprising acetic acid, water and vinyl acetate monomer was introduced via line 15 directly into the preliminary dewatering column 5. (The broken line 16 shows the embodiment customary in the art, in which the bottom product of the water scrubber 9 is transferred into the crude vinyl acetate monomer vessel 17 and then separated in the azeotrope column 19.)
- The top product of the water scrubber 9 was transferred via line 10 into the CO₂ scrubber 11, which, in a conventional manner, possessed a potassium carbonate-filled absorption unit and a desorber. After the CO₂ scrubbing, the cycle gas substream had a CO₂ content of 2% by volume and a pressure of 9 to 11 bar abs. Upstream of the recycling via line 12 into the cycle gas line 14, an ejector 13 was used to inject the entire ethylene feed with a pressure of 20 to 25 bar abs.
- The energy saving in the cycle gas compressor 7 was approx. 1000 MWh per year.

Claims:

1. Process for preparing vinyl acetate monomer in a heterogeneously catalysed, continuous gas phase process by reacting ethylene with acetic acid and oxygen in a reactor, and
 - a) separating the product gas stream comprising essentially ethylene, vinyl acetate monomer, acetic acid, water, carbon dioxide and further inert gases, and
 - b) recycling an ethylene- and CO₂-containing cycle gas stream into the reactor, by
 - c) compressing the cycle gas stream in a cycle gas compressor before recycling into the reactor, and
 - d) branching off a substream of the cycle gas on the suction side or the pressure side of the cycle gas compressor and feeding it to a CO₂ scrubbing, and
 - e) prior to the CO₂ scrubbing, washing it in a water scrubber, characterized in that
 - f) the substream, after the CO₂ scrubbing, is supplied to the cycle gas via a jet compressor, together with ethylene as the motive medium, on the pressure side of the cycle gas compressor and downstream of the withdrawal of the substream to the CO₂ scrubbing, and/or
 - g) the bottom product from the water scrubber is fed directly to the preliminary dewatering column.
2. Process according to Claim 1, characterized in that
 - f) the substream, after the CO₂ scrubbing, is supplied to the cycle gas via a jet compressor, together with ethylene as the motive medium, on the pressure side of the cycle gas compressor and downstream of the withdrawal of the substream to the CO₂ scrubbing,or

g) the bottom product from the water scrubber is fed directly to the preliminary dewatering column.

3. Process according to Claim 1, characterized in that

f) the substream, after the CO₂ scrubbing, is supplied to the cycle gas via a jet compressor, together with ethylene as the motive medium, on the pressure side of the cycle gas compressor and downstream of the withdrawal of the substream to the CO₂ scrubbing,
and

g) the bottom product from the water scrubber is fed directly to the preliminary dewatering column.

4. Process according to Claims 1 to 3, characterized in that the entire ethylene feed which is supplied to the cycle gas stream upstream of the reactor is supplied via the jet compressor.

5. Process according to Claims 1 to 3, characterized in that the bottom product from the water scrubber is heated by means of heat exchange with the cycle gas and is fed to the preliminary dewatering column.