METHOD AND DEVICE FOR PRODUCING VINYL ACETATE

The invention relates to a process and an apparatus for preparing vinyl acetate monomer in a heterogeneously catalysed, continuous gas phase process by reacting ethylene with acetic acid and oxygen in a tube bundle reactor.

Vinyl acetate monomer (VAM) is prepared in a continuous process 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 and alkali metal salts on a support material and may additionally be doped with gold, rhodium or cadmium.

The ethylene, oxygen and acetic acid reactants are reacted in an exothermic reaction (VAM: $\Delta_B H^\circ_{299}$ = - 176 kJ/mol), generally at a pressure of 1 to 30 bar and a temperature of 130°C to 200°C, in a fixed bed tubular reactor to give vinyl acetate monomer:
$C_2H_4 + CH_3COOH + ½\ O_2 \rightarrow CH_3COOCH{=}CH_2 + H_2O$

The main side reaction is the total oxidation of ethylene to CO_2:
$C_2H_4 + 3\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$
The heat of formation here is $\Delta_B H^\circ_{299}$ = - 1324 kJ/mol!
The ethylene conversion is about 10%, the acetic acid conversion 20 to 30%, and the oxygen conversion up to 90%.

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 typically by means of a steam-heated acetic acid saturator or acetic acid evaporator.

After the reaction, the reaction products and unconverted acetic acid are condensed out of the cycle gas and sent to workup. Uncondensed product is scrubbed out in a scrubber operated with acetic acid. The cycle gas or a portion thereof, before being admixed again with the reactants, is purified to free it of carbon dioxide formed. The condensed vinyl acetate monomer and water products, and also unconverted acetic acid, are separated from one another in a multistage distillation process typically operated with steam. The customary distillation steps are dewatering (optionally also preliminary dewatering), azeotropic distillation, pure VAM column, residue workup, and low boiler and high boiler removal.

The reaction temperature in the fixed bed tube bundle reactor, generally from 130°C to 200°C, is set by means of evaporative water cooling at a pressure of 1 to 10 bar. This forms steam, known as in-process steam, generally at a temperature of 120°C to 185°C, at a pressure of 1 to 10 bar, preferably 2.5 to 5 bar. The decline in activity over the operating time of a catalyst is balanced by increasing the reaction temperature, i.e. the operating pressure of the evaporative water cooling. To conserve the catalyst, for the purpose of achieving a maximum service life, and to optimize the ethylene selectivity, by minimizing the CO_2 formation, the vinyl acetate reaction should be conducted for as long as possible with as low as possible a reaction temperature.

In general, the fixed bed tube bundle reactors are formed from several thousand, typically 2000 to 6000,

tightly packed and vertically arranged, cylindrical tubes. For industrial scale use, tubes with a length of 5 to 6 m and an internal diameter of 33 mm to 40 mm are used for this purpose. The surface/volume ratio is generally 100 to 120 m^{-1}.

A problem in vinyl acetate monomer preparation in a heterogeneously catalysed gas phase process, especially given increasingly high-performance catalysts, is the heat of reaction released. This is because the process is characterized by significant exothermicity, to a lesser degree in the main reaction than in the side reaction of ethylene oxidation. Even given good ethylene selectivity values (> 92%), at a molar ratio of VAM: CO_2 of approx. 7:1, owing to the high heat of formation of the CO_2, half of the heat of reaction originates from this side reaction! Even given the constant improvement in VAM catalysts with regard to the space-time yield (STY), it is therefore never possible at the same time also to improve the ethylene selectivity S_E in such a way that, as a result of the increase in STY, the overall exothermicity would also be reduced.

The procedure in the prior art to date has been to compress to a higher degree with higher-performance cycle gas compressors, in order that the flow rate of the cycle gas was increased, and the axial heat removal was optimized. Disadvantages are the higher pressure differences in all cycle gas apparatuses, and the difficulty of controlling the high gas velocity of the cycle gas. For the conventional VAM catalysts, the STY of which is between 400 and 700 g of VAM/l of catalyst x h, such measures, with all the disadvantages mentioned, were sufficient.

In the case of high-performance catalysts for VAM preparation, the STY of which is significantly above

700 g of VAM/l of catalyst x h, the heat of reaction formed is significantly higher, with the consequence that the removal of heat in the steam/water cooling medium, even with the abovementioned measures for increasing the cycle gas velocity, is too slow. The consequences are that there is not just increased occurrence of local temperature increases (hotspots) in the reactor and an associated reduction in ethylene selectivity, but also shortened catalyst service lives and higher by-product formation overall.

EP 1033167 A2 discloses a tube bundle reactor with graduated internal diameter, wherein the tubes in the region of the inlet of the reaction mixture have a smaller diameter than in the region of the outlet of the reaction mixture. The document advises against a general reduction in the diameter of the tubes of a tube bundle reactor, since the manufacturing costs of the reactor (more tubes) would thus increase and the expenditure associated with filling them would rise.

It was an object of the invention to improve the process for preparing vinyl acetate monomer by reacting ethylene with acetic acid and oxygen in a heterogeneously catalysed, continuous gas phase process to the effect that high-performance catalysts with a space-time yield (STY) of more than 700 g of VAM/l of catalyst x hour can be used, with avoidance of local temperature increases (hotspots) and associated reduction in ethylene selectivity.

The invention provides a process for preparing vinyl acetate monomer (VAM) by reacting ethylene with acetic acid and oxygen in a fixed bed tube bundle reactor in a heterogeneously catalysed, continuous gas phase process, characterized in that a high-performance catalyst with a space-time yield of > 700 g of VAM/l of catalyst x hour is used for catalysis, and in that the

fixed bed tube bundle reactor comprises tubes with a ratio of inner surface area to volume of ≥ 130 m^{-1}.

The fixed bed tube bundle reactors used to prepare vinyl acetate monomer consist generally of a cylindrical vessel in which a multitude of cylindrical tubes (the tube bundle) are arranged vertically. The tubes are arranged tightly packed in the bundle. Typically, a fixed bed tube bundle reactor for industrial scale use comprises 2000 to 6000 tubes. In general, the distance between the tubes, i.e. between the central internal axes of the tubes, is 30 to 40 mm. A water/steam mixture as a heat exchange medium flows through the interstices between the tubes themselves, and the tubes and the vessel, for cooling.

The invention further provides an apparatus for performing the process according to the invention, comprising a fixed bed tube bundle reactor with cylindrical tubes with a ratio of inner surface area to volume of ≥ 130 m^{-1}.

Useful reactors for industrial scale use are fixed bed tube bundle reactors with a height of several metres, i.e. generally a tube length of 4 to 7 m. The tubes are steel tubes with a wall thickness of generally 1 to 3 mm. According to the invention, the dimensions of the tubes are such that the ratio thereof of surface area (in the tube interior) to tube volume is ≥ 130 m^{-1}, preferably 130 to 160 m^{-1}. The internal diameter of the tubes is preferably constant over their entire length.

It was found that, compared to the conventional A:V ratio of about 100 to 120 m^{-1}, especially at a surface area/volume ratio of 130 to 160 m^{-1}, improvements with regard to heat removal of > 30% are achievable. Even more significant removal of heat is achievable with significantly smaller tube diameters, but the tube

filling then begins to become uneconomic, or the ever narrower tubes result, in the course of filling, in considerable bridge and gap formations of the catalyst bodies, particularly at the walls. Although this can be counteracted by a reduction in the catalyst particle size, this in turn leads to a reduction in the void volume and hence to a considerable rise in the pressure difference.

For catalysis, the tubes are filled in a known manner with particulate high-performance catalysts with a space-time yield of > 700 g of VAM/l of catalyst x hour, preferably 800 to 1500 g of VAM/l of catalyst x hour, more preferably 900 to 1500 g of VAM/l of catalyst x hour. They are generally supported catalysts based on an inert, inorganic support material such as titanium oxides, silicon oxides, aluminium oxides, which are coated with a palladium compound in combination with alkali metal salts, and may additionally be doped with gold, rhodium or cadmium. The supported catalysts may be present in the form of spheres, cylinders or rings, the dimensions thereof being matched to the tubes used, and they generally have lengths and widths of 3 to 10 mm and diameters of 3 to 6 mm.

The most noticeable improvement in the inventive procedure was the significant increase in ethylene selectivity, and the parallel significant rise in space-time yield (STY). The oxygen selectivity also improved noticeably. Moreover, the values in the tables show that it was possible to employ almost 10% less condensate circulation. Thus, over and above the gain in selectivity and STY, it is also possible to achieve a power saving in the condensate circulation pumps.

Example:

The thermal reaction profile was compared in two tubular reactors equipped with tubes with a diameter of 33 mm (comparative) or tubes with a diameter of 27 mm (inventive).

A) A reactor with four tubes (length 6.30 m, internal diameter 33 mm; A/V = 120 m^{-1}); cooling medium: water/steam with a condensate circulation of 1300 kg/h; external heat removal via a steam drum. One tube equipped with a temperature measurement chain, one measurement point every 20 cm.

B) A reactor with 7 tubes (length 6.30 m, internal diameter 27 mm; A/V = 148 m^{-1}), cooling medium: water/steam with a condensate circulation of 1240 kg/h; external heat removal via a steam drum. Two tubes equipped with a temperature measurement chain, one measurement point every 20 cm.

Both reactors were filled with a VAM catalyst, KL 7900 SH from KataLeuna, Germany (Pd 1.5% by weight; Au 1% by weight). Since the results, in the case of use of the space-time yield (STY = g of VAM/l of catalyst x hour), relate to 1 litre of catalyst, the greater amount of catalyst in the 7-tube reactor is unimportant.

In a VAM pilot plant with the two reactors A and B, identical catalysts were tested under identical reaction conditions.

The reaction conditions, space-time yield and selectivity are shown in Table 1 (after 300 h), Table 2 (after 400 h), Table 3 (after 1000 h) and Table 4 (after 1500 h). The temperature profile in the reactors is shown in Figure 1 (after 300 h), Figure 2 (after 400 h), Figure 3 (after 1000 h) and Figure 4 (after 1500 h).

As early as after 300 hours, a significantly improved temperature profile was found in the inventive procedure. The temperature difference between the comparative reactor and the reactor equipped in accordance with the invention was up to more than 10°C, which became even more clear after an operating time of 400 h. It was thus possible to obtain an increase in the ethylene selectivity of more than 1% in the initial period (300 to 400 h). The advantages became even more clear with increasing experiment time, in spite of another increase in the amount of condensate circulated in the reactor with large tubes, but homogeneous circulation in the case of the 27 mm tubes, i.e. less cooling in the reactor with 27 mm tubes, the ethylene selectivity in the latter improved by 2%.

Table 1: (Conditions and performance after 300 hours)

Tube diameter	**33 mm**	**27 mm**
Cycle gas pressure (p_e)	8.5	8.5
AcOH (%)	12.0	11.5
C_2H_4 (%)	65	65
Temperature (°C)	150	150
O_2 (%)	6.8	6.8
Condensate circulation (kg/h)	1340	1240
GHSV (1/h)	3740	3720
(GHSV = Gas Hourly Space Velocity)		
STY (kg VAM/l cat x h)	850	850
C_2H_4 selectivity	92.1	93.3
O_2 selectivity	65 - 70	75 - 80

Figure 1: Temperature profile of both reactors after 300 h (upper line = tube with diameter 33 mm)

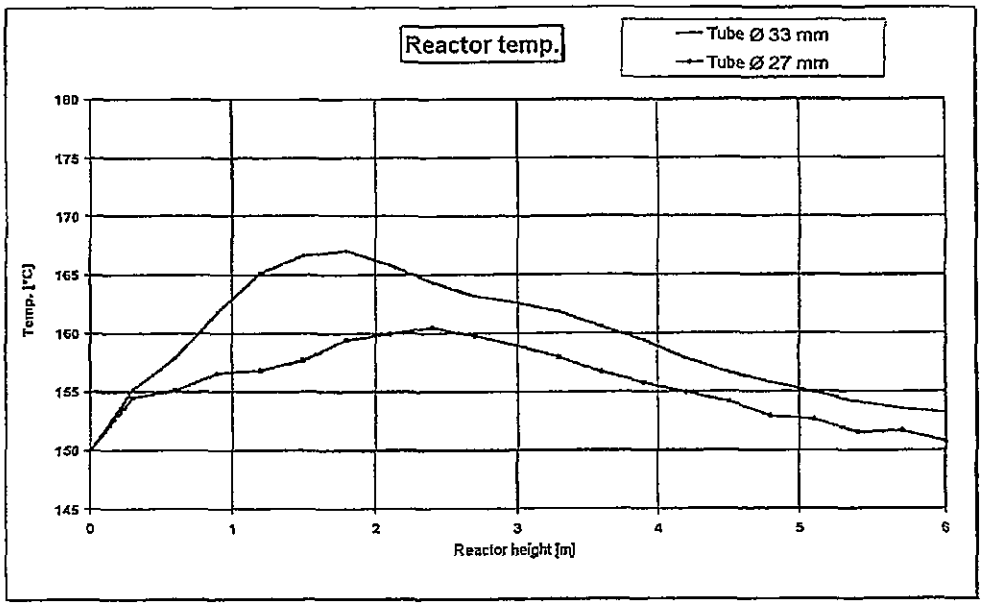


Table 2: (Conditions and performance after 400 hours)

Tube diameter	**33 mm**	**27 mm**
Cycle gas pressure (p_e)	8.5	8.5
AcOH (%)	12.3	11.5
C_2H_4 (%)	65	65
Temperature (°C)	150	150
O_2 (%)	8.6	8.8
Condensate circulation (kg/h)	1340	1240
GHSV (1/h)	3750	3750
STY (kg VAM/l cat x h)	900	935
C_2H_4 selectivity	91.0	92.3
O_2 selectivity	65 - 70	75 - 80

Figure 2: Temperature profile of both reactors after 400 h (upper line = tube with diameter 33 mm)

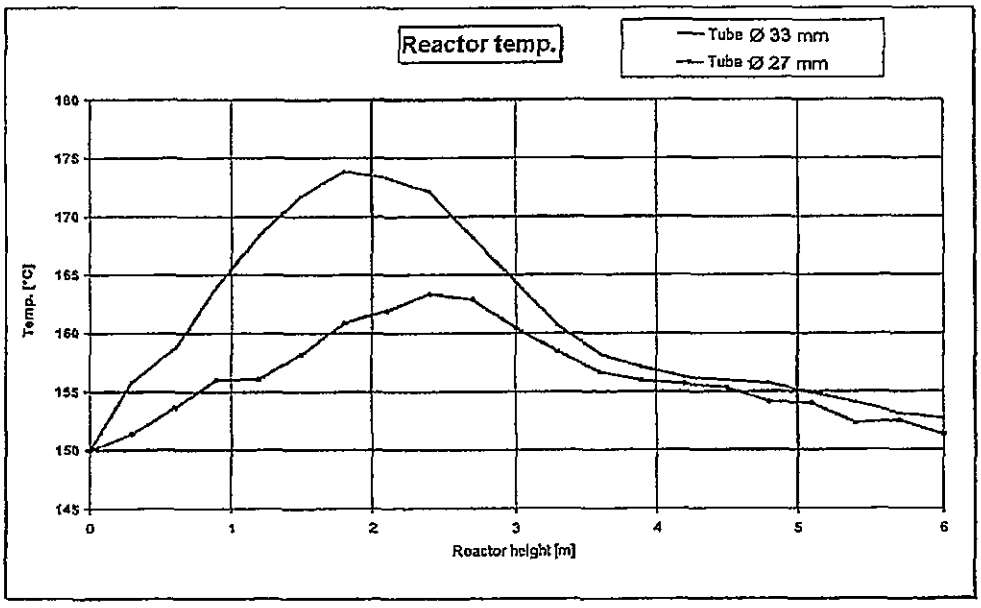


Table 3: (Conditions and performance after 1000 hours)

Tube diameter	**33 mm**	**27 mm**
C_2H_4 (%)	61.3	63.1
Temperature (°C)	150	155
Condensate circulation (kg/h)	1530	1230
GHSV (1/h)	3660	3820
STY (kg VAM/l cat x h)	920	980
C_2H_4 selectivity	90.9	93.3
O_2 selectivity	55 - 60	65 - 70

Figure 3: (conditions and performance after 1000 hours) (upper line = tube with diameter 33 mm)

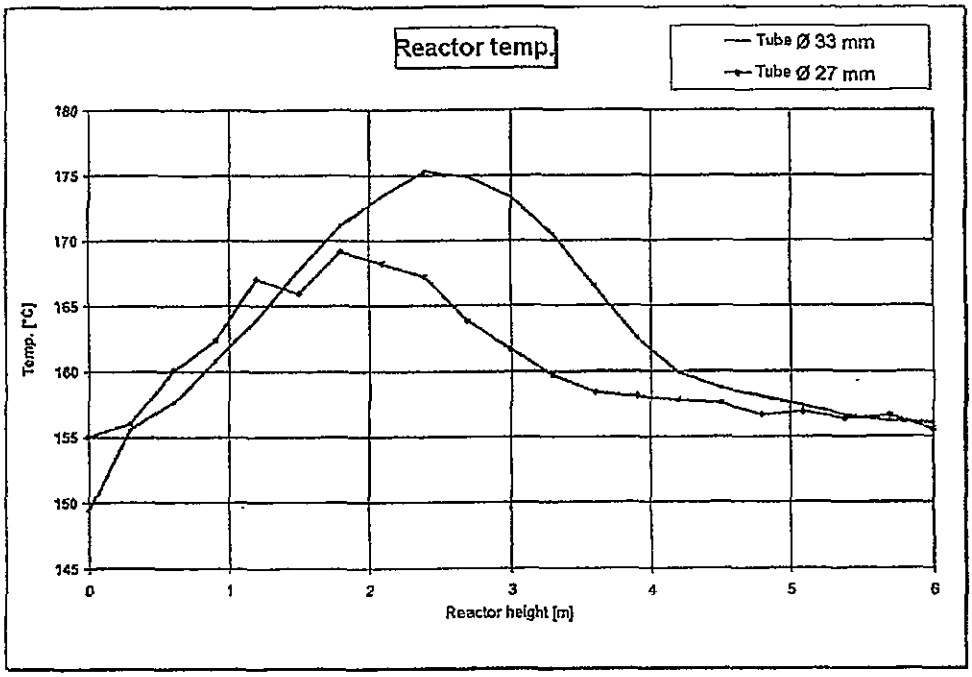
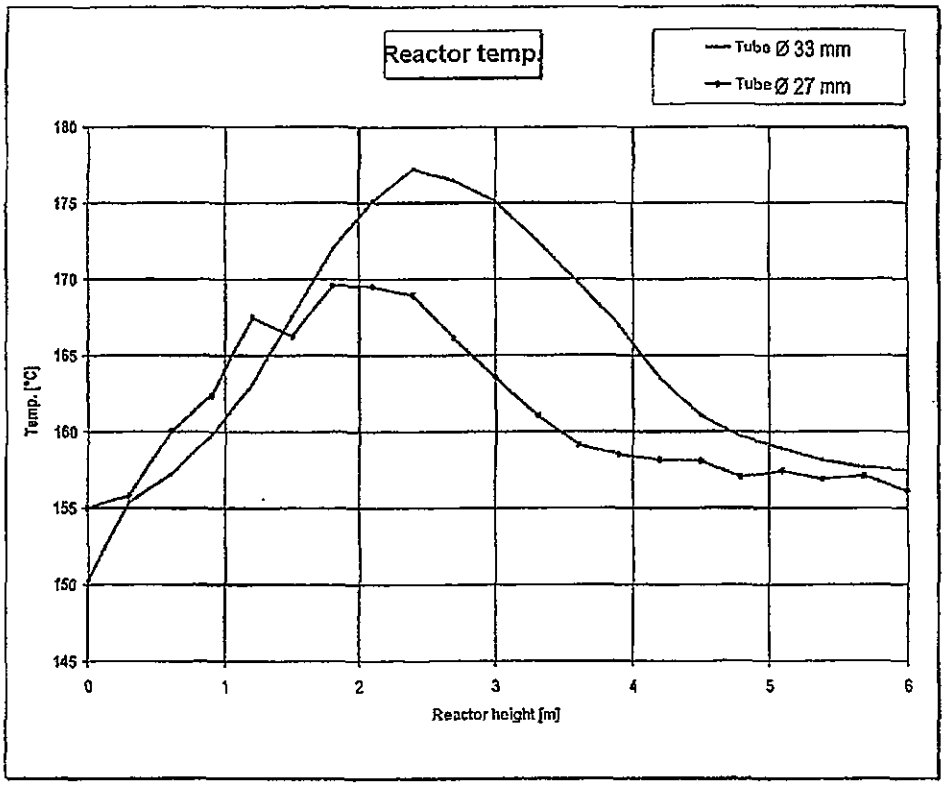


Table 4: (Conditions and performance after 1500 hours)

Tube diameter	**33 mm**	**27 mm**
C_2H_4 (%)	61.0	62.0
Temperature (°C)	150	155
Condensate circulation (kg/h)	1750	1260
GHSV (1/h)	3600	3800
STY (kg VAM/l cat x h)	930	980
C_2H_4 selectivity	91.4	93.4
O_2 selectivity	60 - 65	70 - 75

Figure 4: (conditions and performance after 1500 hours)
(upper line = tube with diameter 33 mm)



Claims:

1. Process for preparing vinyl acetate monomer (VAM) by reacting ethylene with acetic acid and oxygen in a tube bundle reactor in a heterogeneously catalysed, continuous gas phase process, characterized in that a high-performance catalyst with a space-time yield of more than 700 g of VAM/l of catalyst x hour is used for catalysis, and in that the tube bundle reactor comprises tubes with a ratio of inner surface area to volume of $\geq 130\ m^{-1}$.

2. Process according to Claim 1, characterized in that the ratio of inner surface area to volume is from 130 to 160 m^{-1}.

3. Process according to Claim 1 or 2, characterized in that the tube bundle reactor comprises tubes with a tube length of 4 metres to 7 metres.

4. Process according to Claims 1 to 3, characterized in that a water/steam mixture as a heat exchange medium flows through the tube bundle reactor for cooling.