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Production of a homogeneous mixture of a gaseous aromatic hydrocarbon and an oxygen-containing gas /



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- 5 The present invention relates to a process and an apparatus for producing a homogeneous mixture of a gaseous aromatic hydrocarbon and an oxygen-containing gas for catalytic gas-phase reactions, in particular a homogeneous mixture of gaseous o-xylene and/or naphthalene and air for the preparation of phthalic anhydride.
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- Phthalic anhydride (PA) is an important intermediate for producing synthetic resins, phthalate plasticizers, phthalocyanine dyes and further fine chemicals. PA is nowadays prepared primarily from o-xylene, predominantly by gas-phase oxidation of o-xylene by means of air as oxidant.
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- Plants for carrying out such a PA production process consist essentially of the functional units for producing the o-xylene vapor/air mixture, the reactor for reacting the o-xylene vapor/air mixture and a facility for separating off and working up the PA.
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- The catalytic gas-phase oxidation reaction is usually carried out over V_2O_5 -containing catalysts. For this purpose, o-xylene is vaporized, mixed with an excess of air and passed at from 340°C to 440°C over the catalyst in the tubes of a shell-and-tube reactor. The catalyst comprises, for example, a mixture of V_2O_5 and TiO_2 with promoters on ceramic bodies, e.g. porcelain or SiC spheres or rings having dimensions of, for example, 6 x 6 mm. Large reactors have from 10 000 to 40 000 tubes arranged within the shell. The o-xylene is usually oxidized to PA with a selectivity of from 78% to 80%. This oxidation itself is strongly exothermic, with an enthalpy change of -1110 kJ/mol.
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- In carrying out the process, attention has to be paid, inter alia, to the following critical points: firstly, the mixture of o-xylene with air (oxygen excess) is in the explosive range (Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, volume A 20, page 85), and, secondly, the flow of the gas mixture into each of the large number of 10 000 - 40 000 tubes has to be uniform over the entire cross section and constant over time so that the reaction proceeds equally quickly in all tubes and not, for instance, particularly quickly or particularly slowly in some of them. In addition, the high negative enthalpy of reaction can lead to the catalyst sintering, melting or becoming inactive in individual tubes if deviations from the set conditions occur.
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This is associated with considerable risks for the plant.

Furthermore, inhomogeneities in the supply of gas mixture result in different reaction conditions in the individual tubes. This
5 causes increased formation of by-products which reduce the yield and have to be separated from the PA in later purification stages and disposed of.

10 DE-A 1 793 453 discloses a process for producing a homogeneous mixture of gaseous o-xylene and air for the catalytic oxidation to phthalic anhydride. In the known process, a stream of o-xylene is atomized to form droplets having a diameter of less than 1 mm, for example a size of predominantly below 0.3 mm, and introduced
15 into a stream of air which has been preheated to above the boiling point of o-xylene. This stream of air is turbulent; a Reynolds number of above 200 000 is recommended. The residence time from injection of the o-xylene to the reactor has to be at least 0.2 seconds so as to obtain a homogeneous gas mixture and thus uniform flow into all tubes.
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Despite this improvement provided by the process of DE-A 1 793 453, changes in the droplet size and problems in vaporization can take place, particularly if the operating
25 conditions fluctuate. This could be due to a number of possible causes:

The raw materials can have a varying level of contamination. The air can contain, inter alia, NO_x , H_2S , sulfur oxides such as SO_2 ,
30 NH_3 and its salts, e.g. with CO_2 , which can lead to constriction of one or more nozzles. Corrosion particles can also change the droplet size and shape of the atomized o-xylene jet. Similar effects are caused by erosion of the nozzles in long-term operation. Furthermore, the o-xylene can also contain m- and
35 p-xylene, toluene, ethylbenzene, isopropylbenzene, nonane and small amounts of styrene. Such compounds can influence the surface tension of the o-xylene. It is possible for droplets which fly further than the abovementioned droplets having a size of, for example, predominantly below 0.3 mm to be formed. These
40 can wet the wall of the reaction tube and form a liquid film there. An additional difficulty is that it is not possible in practice to install the nozzles serving for atomization of the o-xylene stream in such a way that no droplets of the atomized o-xylene stream come into contact with the wall of the guide
45 tube.

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In addition, unintentional, adverse changes in the set parameters such as pressure and temperature and the quantity of air can occur in the process of DE-A 1 793 453. Furthermore, contaminants present in the starting materials air and o-xylene can be introduced and the droplets of the atomized o-xylene stream can touch the wall of the tube. In these respects, the abovementioned process is still in need of improvement.

It is an object of the present invention to provide an improved process and an apparatus for producing a homogeneous mixture of a gaseous aromatic hydrocarbon, e.g. o-xylene and/or naphthalene, and an oxygen-containing gas, in particular air, for catalytic gas-phase reactions. In particular, the above-described disadvantages should be avoided or at least minimized.

We have found that this object is achieved by, in a process of this type, carrying out the atomization of the liquid aromatic hydrocarbon by means of a nozzle which forms a hollow atomization cone, preferably a swirl nozzle. The hollow atomization cone can initially be a coherent film of the liquid hydrocarbon which at a greater distance from the swirl nozzle breaks up into small fragments which are transformed by surface forces into individual droplets having a diameter of less than 1 mm.

The present invention accordingly provides a process for producing a homogeneous mixture of a gaseous aromatic hydrocarbon, e.g. o-xylene and/or naphthalene, and an oxygen-containing gas, e.g. air, for catalytic gas-phase reactions, by atomizing the liquid aromatic hydrocarbon to form droplets having a diameter of less than 1 mm and injecting it into an oxygen-containing gas stream preheated to above the boiling point of the aromatic hydrocarbon, wherein the liquid aromatic hydrocarbon is atomized by means of nozzles which form a hollow cone, preferably by means of swirl nozzles.

The process of the present invention makes it possible to produce a very homogeneous, streaming-free mixture of gaseous oxygen, preferably in air or another oxygen-containing gas, and a hydrocarbon vapor.

The process of the present invention is preferably used in the preparation of carboxylic acids or carboxylic anhydrides by catalytic gas-phase oxidation of aromatic hydrocarbons, for example, xylenes, in particular o-xylene and/or naphthalene, in fixed-bed reactors. An example which may be mentioned is the

preparation of phthalic anhydride (PA).

- In the following, reference is made, purely by way of example, to the particularly preferred use of the process of the present invention in the preparation of PA by catalytic gas-phase oxidation. Here, the aromatic hydrocarbon is o-xylene and the oxygen-containing gas is air.
- 10 In the process of the present invention, the hollow atomization cone preferably has an opening angle of from 30° to 70° . The hollow atomization cone particularly preferably has an opening angle of about 60° .
- 15 The axis of the hollow atomization cone is aligned in the flow direction of the oxygen-containing gas, i.e., for instance, the air, but can deviate by up to 30° from this. This means that the central axis of the hollow atomization cone of the hydrocarbon stream is at an angle of from -30° to $+30^\circ$ to the central axis of the preheated gas stream. As a result, fewer droplets of the hollow cone touch the wall. A further measure to achieve this can be, in particular, to maintain a certain distance, for instance one third of the tube radius, from the wall. Preference is given to using a plurality of nozzles, for instance from 2 to 6, preferably from 4 to 6, with approximately equal spacing.

- According to the present invention, preference is given to using swirl nozzles for atomizing the liquid hydrocarbon. These swirl nozzles, also referred to as hollow cone nozzles, preferably have, upstream of the outlet orifice, a guide body having oblique impingement surfaces which impart a swirl or rotation about the flow axis to the liquid to be atomized. Such swirl nozzles are known for other applications, for example rapid impulse transmission in water jet pumps, spray condensers, etc. (cf. Grassmann "Physikalische Grundlagen der Verfahrenstechnik", Verlag Sauerländer (1970), pages 355 and 805). Although the use of hollow cone nozzles is particularly preferred in the process of the present invention, solid cone nozzles or slit nozzles can also be used in other embodiments of the invention. The use of two-fluid nozzles which can be supplied, for example, with the o-xylene to be sprayed and the propellant air is also possible.

- If a swirl or hollow cone nozzle is used for generating the hollow atomization cone according to the present invention, this is preferably operated at an admission pressure of from 2 to 20 bar so as to ensure that a hollow atomization cone having the opening angle of from 30° to 70° preferred according to the

present invention is formed.

In the process of the present invention, the liquid hydrocarbon stream is atomized to form droplets having a diameter of less than 1 mm, preferably less than 0.8 mm. The liquid stream is particularly preferably atomized to form droplets of from 0.02 to 0.2 mm.

The swirl nozzles used to form the hollow atomization cone having an opening angle of from 30° to 70° are advantageously located within a tube through which the oxygen gas flows in a circular arrangement on a tube having an inlet for the liquid to be atomized. However, the annular feed tube for the liquid can also be arranged around the oxygen feed tube and the nozzles can be passed from the outside into the oxygen feed tube. In this case, the nozzle outlet orifices are directed in the direction of gas flow. However, as already stated above, the axis of the hollow cone can deviate by up to 30° from the flow direction of the gas. This can reduce the number of droplets of the hollow cone which touch the wall.

For the purposes of the process of the present invention, KS 1 axial hollow cone nozzles (from Lechler, Metzingen, Germany) are particularly suitable. Such nozzles make it possible to generate a hollow cone having the preferred cone angle of 60°. The hollow cone diameter is then about 200 mm at a distance of 250 mm from the outlet orifice. According to the present invention, small droplets having a diameter of less than 1 mm, preferably less than 0.8 mm, particularly preferably from 0.02 to 0.2 mm, are formed. The latter vaporize very quickly and are completely vaporized at a distance of only 200 - 500 mm from the outlet orifice of the nozzle. However, droplets having a size of from 0.8 to 1 mm can fly 50 - 100 cm before they are completely vaporized and can thus touch and wet the wall.

Because of this possibility of wetting, a particularly preferred embodiment of the process of the present invention provides for the mixture, for example the o-xylene/air mixture, to be produced in a chamber which is bounded by side walls heated to above the boiling point of the hydrocarbon. The side walls of the chamber are preferably formed by a heated tube, for instance a double-walled tube, in particular a "Thermoblech" (= commercial double-walled metal sheet) tube (such "Thermoblech" tubes are manufactured in Germany by, for example, the companies BUCO, Geesthacht, or DEG, Gelsenkirchen). Hydrocarbon droplets which impinge on the heated tube cannot deposit as a liquid film but instead are immediately vaporized. This finally produces the

desired mixture of hydrocarbon vapor and, for example, air.

The annular gap of the double-walled tube can be heated by high-pressure steam, preferably steam having a pressure of about 20 bar and a temperature of 214°C. The abovementioned "Thermoblech" tubes can have a particularly narrow annular gap. "Thermoblech" tubes have a relatively simple construction and are therefore relatively inexpensive. Intensive heating enables cold spots to be ruled out in "Thermoblech" tubes.

To achieve complete homogenization, the vapor/air mixture is, in a further advantageous process variant, subsequently passed through a mixing device.

Preference is given to using static mixers. These are guide plates which are installed in the tube through which flow occurs and which divide and recombine the stream to be mixed, resulting in complete homogenization. Such static mixers are manufactured by, for example, Sulzer, Winterthur, Switzerland. Static mixers are also described in the German Patent Applications DE 25 250 20 A1, DE 196 223 051 A1 and DE 196 23 105 A1.

The present invention also provides an apparatus for producing a homogeneous mixture of a gaseous aromatic hydrocarbon and an oxygen-containing gas having gas channels for a preheated, oxygen-containing gas stream and an atomization device for a stream of a liquid aromatic hydrocarbon opening into the gas channels, wherein the atomization device has swirl nozzles and the gas channels have, at least downstream of the swirl nozzles, walls which can be heated to at least the boiling point of the hydrocarbon.

The gas channels preferably comprise a heatable tube, in particular a double-walled tube or a tube of "Thermoblech". Particularly preferably, there is a static mixer installed in the gas channels downstream of the swirl nozzles.

The temperature at the hot tube wall is set so that from 5 to 50% by weight of the liquid hydrocarbon, in particular from 5 to 40% by weight, particularly preferably from 5 to 30% by weight, can impinge on the tube wall and be vaporized there, with the precise proportion depending on the impurities in the raw materials, on the shape of the hollow cone and on changes in the nozzle (erosion) during operation.

The abovementioned functional unit can be followed by further functional units for, for example, preparing PA, e.g. the reactor for converting the o-xylene into PA and the apparatus for separating off PA and isolating pure PA, as are known from the prior art.

The invention is illustrated below with the aid of an embodiment shown schematically in the attached drawing and by a use example.

10 The figure shows an apparatus 10 for producing a homogeneous mixture of gaseous o-xylene and/or naphthalene and air. The apparatus has gas channels 11 which conduct a preheated stream of air (symbolized by the arrow 12 in the figure). In the example shown, the gas channels 11 are configured as tubes. The tube 11 is provided with an atomization device 13 which comprises feed lines 14 for liquid o-xylene and swirl nozzles 15 located at the end of the lines. The feed lines 14 are fed by a supply tube (not shown) which concentrically surrounds the tube 11. The swirl nozzles 15 produce a hollow cone 16 of liquid o-xylene which breaks up into very fine droplets having a mean diameter of from 0.02 to 0.2 mm. The fine droplets vaporize very quickly in the preheated air stream, so that a homogeneous mixture of air and o-xylene vapor is formed. To improve the homogeneity further, a static mixer 17 is installed in the tube 11 so that the vapor/air mixture is passed through this mixer. Downstream of the swirl nozzles 15, the tube 11 is configured as a heatable double-walled tube 18. The tube is heated by means of steam to a temperature above the boiling point of o-xylene. Droplets of atomized o-xylene which impinge on the tube wall are thus vaporized immediately and do not deposit as a liquid film. At the point 19, the tube 11 opens into a shell-and-tube reactor in which phthalic anhydride is prepared by catalytic gas-phase oxidation of the o-xylene.

35 Example

In a plant for preparing PA, the apparatus for vaporizing o-xylene comprised a vertical "Thermoblech" tube having a diameter of 1200 mm. The oxidation air, which had been preheated to 200°C in a preheating apparatus, was conveyed through this to the reactor. The pressure was about 1.5 bar absolute. The air was loaded with 100 g of o-xylene per standard m³. The air was drawn in from the surroundings without particular purification, merely through an air filter. The "Thermoblech" tube was heated to 214°C by means of 20 bar steam. The o-xylene was injected via six swirl nozzles which were arranged in a circle having a diameter of 600 mm and whose axis pointed vertically upward. These were axial

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hollow cone nozzles (KS 1 of the type 216.324 made of steel, from Lechler). The admission pressure was 8 bar. Static mixers were installed at a distance of 4.5 m downstream of the nozzles in a horizontal section of tube.

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This swirl nozzle/hot wall mixer system produced a homogeneous, streaming-free o-xylene vapor/air mixture whose homogeneity was not upset by fluctuating operating parameters. This was established by means of the PA output which was constant over a long period of time. In addition, no ignitions within the production plant caused by inhomogeneities in the mixture and adversely affecting plant safety were observed. Damage or emergency shutdowns due to high temperatures in individual reactor regions or in reactor tubes were not observed. Between the annual routine maintenance shutdowns, the plant availability was above 99%.

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We claim:

1. A process for producing a homogeneous mixture of a gaseous aromatic hydrocarbon and an oxygen-containing gas for catalytic gas-phase reactions, by atomizing the liquid aromatic hydrocarbon to form droplets having a diameter of less than 1 mm and injecting it into an oxygen-containing gas stream preheated to above the boiling point of the aromatic hydrocarbon, wherein the liquid aromatic hydrocarbon is atomized by means of nozzles which form a hollow cone, preferably swirl nozzles.
2. A process as claimed in claim 1, wherein the hollow atomization cone has an opening angle of from 30° to 70° .
3. A process as claimed in claim 1 or 2, wherein the central axis of the hollow atomization cone is at an angle of from -30° to $+30^{\circ}$ to the central axis of the preheated gas stream.
4. A process as claimed in any of claims 1 to 3, wherein the mixture is produced in a chamber which is bounded by side walls heated to above the boiling point of the hydrocarbon.
5. A process as claimed in claim 4, wherein the side walls of the chamber are formed by a heated tube, in particular a "Thermoblech" tube.
6. A process as claimed in claim 4 or 5, wherein from 5 to 50% by weight, preferably from 5 to 40% by weight, particularly preferably from 5 to 30% by weight, of the atomized hydrocarbon are vaporized on the heated side walls.
7. A process as claimed in any of the preceding claims, wherein the mixture after vaporization of the aromatic hydrocarbon is passed through a static mixer.
8. A process as claimed in any of the preceding claims for use in the synthesis of phthalic anhydride, where the aromatic hydrocarbon is o-xylene and/or naphthalene and the oxygen-containing gas is air.
9. An apparatus for producing a homogeneous mixture of a gaseous aromatic hydrocarbon and an oxygen-containing gas having gas channels (11) for a preheated, oxygen-containing gas stream (12) and

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an atomization device (13) for a stream of a liquid aromatic hydrocarbon opening into the gas channels (11), wherein the atomization device (13) has swirl nozzles (15) and the gas channels (11) have, at least downstream of the swirl nozzles (15), walls (18) which can be heated to at least the boiling point of the hydrocarbon.

10. An apparatus as claimed in claim 9, wherein the gas channels (11) comprise a heatable tube, in particular a double-walled tube or a tube made of "Thermoblech".

11. An apparatus as claimed in claim 9 or 10, wherein a static mixer is installed in the gas channels downstream of the swirl nozzles.
