recycled lower alcohol (% by weight)] : [the amount of the non-recycled lower alcohol (% by weight)]) is controlled within the range of 10:0 to 10:10, and it is more preferable that the mixing ratio is controlled within the range of 10:0 to 10:2.

As a method of controlling the amount of water, ammonia and amines, a method in which the amount of water, ammonia and amines are controlled by supplying a non-recycled lower alcohol ~~in~~ into a reaction system, while the amount of water, ammonia and amines are detected in a gas phase reaction, can be mentioned.

The amount of water can be measured by a conventional method such as Karl Fischer's method, and the amount of ammonia and amines can be measured by an ion chromatography method.

[0041]

In the present invention, a molecular oxygen-containing gas may be present in a reaction system. As a molecular oxygen-containing gas, air is preferable in economic terms. The concentration of the molecular oxygen is preferably out of an explosion composition range.

[0042]

The amount of the molecular oxygen in a reaction system during a gas phase reaction is preferably 0.1 to 10 moles, and more preferably 0.3 to 5 moles, relative to 1 mole of cyclohexanone oxime.

[0043]

A gas phase reaction can be generally conducted as a gas phase catalytic reaction in a fixed bed system, a fluidized bed system or a moving bed system. Cyclohexanone oxime as a raw material is reacted in a gas state by being allowed to come into contact with a catalyst layer. A lower alcohol may be mixed with cyclohexanone oxime in advance in a gas state, or may be supplied separately from cyclohexanone oxime. In the case of a fixed bed system, it is preferable that a mixture in which cyclohexanone oxime and a lower alcohol have been mixed well is passed through a catalyst layer. On the other hand, in the case of a fluidized bed system, there is no need to mix cylohexanone oxime and a lower alcohol in advance, and cylohexanone oxime and a lower alcohol may be supplied separately to a reactor vessel. Alternatively, the lower alcohol may be supplied in several batches. In the case of a fluidized bed system, a lower alcohol may be supplied on upper stream side relative to cylohexanone oxime.

[0044]

CLAIMS

1. A method of producing ε-caprolactam, comprising:

conducting a gas phase reaction in which cyclohexanone oxime is allowed to come into contact with a solid catalyst in the presence of a lower alcohol, and then cyclohexanone oxime is converted into ε-caprolactam, and

adjusting the amount of water, ammonia and amines in a gas phase reaction system to the following values (1) to (3) by supplying a gas of a non-recycled lower alcohol into a gas phase reaction system while detecting the amount of water, ammonia and amines in the gas phase reaction, wherein

the lower alcohol comprises a recycled lower alcohol which is recovered from a reaction mixture obtained by a gas phase reaction, and

the mass ratio of the recycled lower alcohol and the non-recycled lower alcohol, represented by [the amount of the recycled lower alcohol] : [the amount of the non-recycled lower alcohol], is within a range of 10:0 to 10:10.

(1) $0 \leq \{[\text{the amount of ammonia (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 14$

(2) $0 < \{[\text{the amount of water (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 11$

(3) $0 \leq \{[\text{the amount of amines (number of moles)} / \text{the amount of the lower alcohol (number of moles)} \times 100]\} < 7.5$

2. The method of producing ε-caprolactam according to claim 1, wherein

the recycled lower alcohol contains a distilled lower alcohol, and wherein

the distilled lower alcohol is obtained by a method which comprises

distilling the reaction mixture obtained by a gas phase reaction to separate gas mainly containing the lower alcohol, then

cooling and condensing part of the gas to obtain a liquid mixture mainly containing the lower alcohol, and then

distilling the liquid mixture to obtain the distilled lower alcohol.

a reaction step of contacting the raw material gas with a solid catalyst to conduct a gas phase reaction, and then converting cyclohexanone oxime into ε-caprolactam to obtain a reaction gas comprising ε-caprolactam, the lower alcohol and the inert gas;

a first distillation step of cooling the reaction gas to obtain a reaction solution, and then separating a high-boiling component from the reaction solution to obtain a mixed gas comprising ε-caprolactam, the lower alcohol and the inert gas;

a lower alcohol separation step of separating a crude lower alcohol mixture containing a lower alcohol and the inert gas, and a crude ε-caprolactam mixture containing ε-caprolactam from the mixed gas;

a second distillation step of separating a low-boiling component and a high-boiling component from the crude ε-caprolactam mixture to obtain ε-caprolactam mixture; and

a lower alcohol recycle step of purifying part or all of the crude lower alcohol mixture to obtain the recycled lower alcohol, wherein

the method of producing ε-caprolactam further comprises adjusting the amount of water, ammonia and amines in the gas phase reaction to the following values (1) to (3) by supplying a gas of a non-recycled lower alcohol into a ~~gas-phase~~ reaction system while detecting the amount of water, ammonia and amines in the gas phase reaction, and

the mass ratio of a recycled lower alcohol and a non-recycled lower alcohol, represented by [the amount of the recycled lower alcohol] : [the amount of the non-recycled lower alcohol], is within a range of 10:0 to 10:10.

(1) $0 \leq \{[$the amount of ammonia (number of moles) / the amount of the lower alcohol (number of moles) $\times 100]\} < 14$

(2) $0 < \{[$the amount of water (number of moles) / the amount of the lower alcohol (number of moles) $\times 100]\} < 11$

(3) $0 \leq \{[$the amount of amines (number of moles) / the amount of the lower alcohol (number of moles) $\times 100]\} < 7.5$

5. The method of producing ε-caprolactam according to claim 4, wherein

the solid catalyst is zeolite.