HU000033248T2

(19) **HU**

(11) Lajstromszám: **E 033 248**

(13) **T2**

MAGYARORSZÁG
Szellemi Tulajdon Nemzeti Hivatala

EURÓPAI SZABADALOM
SZÖVEGÉNEK FORDÍTÁSA

(21) Magyar ügyszám: **E 06 010016**
(22) A bejelentés napja: **2006. 05. 16.**

(51) Int. Cl.: ***B01D 3/00*** *(2006.01)*
C07C 17/02 *(2006.01)*
B01J 19/00 *(2006.01)*

(96) Az európai bejelentés bejelentési száma:
EP 20060010016
(97) Az európai bejelentés közzétételi adatai:
EP 1857430 A1 **2007. 11. 21.**
(97) Az európai szabadalom megadásának meghirdetési adatai:
EP 1857430 B1 **2016. 12. 21.**

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(54) **Továbbfejlesztett eljárás etilén közvetlen klórozása céljából 1,2-diklóretánná**

EP 1 857 430 B1

Improved process for direct chlorination of ethylene to 1,2-dichloroethane

Description

The present invention relates to an improved method for producing dichloroethane and an arrangement for carrying out said method.

Concerning the production of dichloroethane, a distinction is made between two main synthesis paths. While in the so-called direct chlorination process (DC) the reaction product of ethylene and chlorine is produced, the same product is obtained from HCl, O_2 and ethylene in the so-called oxychlorination process (OC). The oxygen in the latter process is not only necessary with respect to reaction technology but also serves for the reactivation and the preservation of the flowability of the catalyst used.

The main area of use of the dichloroethane produced in this way is processing it into vinyl chloride (VCM) and gaseous hydrogen chloride (HCl) by thermal decomposition. The vinyl chloride serves as a starting material for the polymerization into polyvinyl chloride (PVC). The HCl produced is often further processed in an oxychlorination plant. The balanced use of all three reaction steps represents the often cited "Balanced Process".

In the direct chlorination process a distinction is made between a low-temperature process (Low Temperature Chlorination (LTC)) and a high-temperature process (High Temperature Chlorination (HTC)).

While the LTC process is operated at 20–70 °C, the HTC process is carried out at temperatures of 85–200 °C.

The LTC process has the advantage that it works more selectively, it is, however, energetically much less favorable. For example, for the subsequent distillation additional heat needs to be supplied.

The HTC process, however, is basically a little less selective, but in exchange uses the heat of reaction to support the distillative separation subsequent to the reaction.

With respect to selectivity, by using very selective catalysts, it is meanwhile possible to push the HTC process into the range of the LTC process (> 99 %). Therefore, these days virtually exclusively the HTC process is technically used.

But also in the HTC process there are further improvements possible. Since the heat of reaction is approximately 6 times higher than the enthalpy of vaporization, the heat of reaction generated is not needed in its entirety for the subsequent distillation. Even simple distillation devices achieve a dichloroethane purity of > 99.9 % with a reflux ratio of ~1. Thus, more than half of the heat of reaction remains unused. This quantity of heat can be put to a reasonable use inside or outside the process.

To ensure a high yield of dichloroethane, the subsequent reaction into higher chlorinated compounds should be suppressed as possible. For this, the ethylene is contacted with the other reactant, chlorine, as intensely as possible. The unfavorable contact between dichloroethane, used as a solvent, and chlorine has accordingly to be adjusted as precise as possible and kept to a minimum.

In some patent specifications (e.g. DE 4 133 810 A1, DE 0 080 098, EP-A 0 471 987), contrary to this level of knowledge, chlorine and ethylene are added first, which most likely leads to an increased formation of an unwanted amount of high-boilers.

The reaction control is also often described in the art. Here, it is partially considered necessary to carry out the reaction in a loop reactor in order to achieve a satisfying yield (DE 0 080 098). When employing the method according to the present invention described herein, this necessity does not seem to exist.

Another topic is the waste heat that is generated during the reaction. For instance, in the application DE-A 199 10 964, the combination of "closed-cycle operation" and waste-heat utilization is described.

US 4,774,372 discloses a method for producing dichloroethane from ethylene and chlorine with a high selectivity.

The object of the present invention was to provide an improved and a more customized process control of the direct chlorination process and a better utilization of the generated energy.

This object is achieved by a method for producing 1,2-dichloroethane (DCE), comprising feeding ethylene and chlorine into a reactor filled with dichloroethane and having a distillation column fitted thereon, and a system for recovery of heat, wherein the conversion of ethylene and chlorine into dichloroethane is carried out at a temperature of 80 to 130 °C and an absolute pressure of 0.8 to 5 bar, the reaction mixture is kept boiling and the heat of reaction from the reaction mixture is partially removed by using at least one heat exchanger, characterized in that said method is carried out with a device which comprises, (a) as a reactor, a reactor R1 having an arrangement of an external circuit P1 with a heat exchanger W1, and, (b) as a distillation column fitted thereon, a column K1 having an arrangement of an external circuit with a heat exchanger W2.

Another object of the present application is a device for carrying out a method, characterized in that said device comprises

(a) a reactor R1, having an arrangement of an external circuit P1 with a heat exchanger W1, and
(b) a distillation column K1 fitted thereon, having an arrangement of an external circuit with a heat exchanger W2.

Also an object of the present invention is a method for the direct chlorination of ethylene into dichloroethane by using a reactor that allows for a sequential addition of ethylene and chlorine, having a column attached on top of the reactor and at least one external heat removal system as shown in Fig. 1. According to the invention, the reaction can take place in a reactor R1 with a sequential addition of the reactants ethylene and chlorine, using dichloroethane as a solvent, and a catalyst. Caused by the locally generated heat of

reaction, an upward flow inside the reactor occurs that is induced by differences in density.

For a good selectivity with respect to dichloroethane it is favorable that ethylene is added to the reaction mixture (dichloroethane and catalyst) in a dissolved form or at least highly dispersed. In this way there is always a desired reactant available for the subsequently added chlorine. If there is, in contrast, no free ethylene available, the chlorine may react with the dichloroethane to give high-boilers.

The reactants ethylene and chlorine may be diluted by inert gases. As a catalyst, it is recommendable to use ferric chloride modified with sodium chloride, and, as an inhibitor for preventing the generation of by-products, oxygen is preferably used.

The circulation of the liquid medium inside the reactor can, for example, be achieved by a pump and/or according to the thermosiphon or mammoth pump principle, respectively. The circulation velocity of the liquid medium in the mixing zone should not be less than 0.1 m/s. The circulation toward heat exchange and product evaporation may as well be carried out by pump and/or according to the thermosiphon principle; it is even possible to carry out both processes being connected in series within a single circuit of liquid medium.

Under typical reaction conditions of temperatures of 116 °C and absolute pressures of 2 bar, reaction selectivities of 99.7 % can be achieved.

The reaction conditions given herein serve as examples and describe a preferred embodiment of the invention, but should not be construed as limiting the invention.

The attached column K1 offers the advantage that the heat of reaction generated in reactor R1 can directly and without any heat exchange be employed for the distillation that follows the reaction. In this way, low-boilers and volatile compounds can be withdrawn from the process via line 1, the purified final product via line 2, and high-boilers via line 3.

Via a circuit P1 the heat of reaction from reactor R1 may partially be fed to heat exchanger W1. Said heat exchanger W1 may, for example, transmit the heat either to another process medium—of the same or of a different plant—that has to be preheated for use in this or any other process, or, alternatively, water may be processed into low-pressure vapor or into hot water and put to a reasonable energetic use.

A pressurized ethylene-driven gas ejector may also be employed as the circulation device P1. There are no moving parts here that might be damaged by cavitation, and an intense mixing of the reaction mixture with ethylene occurs, which has a positive influence on selectivity.

By combining the distillation column K1, attached on top of the reactor R1, with the external heat exchangers W1 and, optionally, W2 for recovery of heat, many operational states of the reactor can be set. When operated with a high dichloroethane selectivity of the reaction and/or low expectations as to the purity of the dichloroethane, a lot of heat can be removed via heat exchanger W1 and put to further use. If the reaction runs under low dichloroethane selectivity, or if dichloroethane with a higher purity should be fed via line 2, more heat is preferably removed via heat exchanger W2 at the top of distillation column K1, and less heat via heat exchanger W1. By removing heat at the top of the distillation column, the reflux ratio inside the distillation column is increased and its purification efficiency is improved.

For example, very high dichloroethane purity (> 99.9 %) is necessary to allow for a low formation of soot in the dichloroethane cracker when processing it into VCM. The cause for the necessity of a higher purity may be the use of ethylene having a lower purity, or reaction problems, for example, with the catalyst charged into reactor R1.

Figures:

Figure 1 shows an arrangement of a device for carrying out the method of the present invention with a reactor R1 into which the reactants of the reactions are fed, which has an external circuit P1 with a heat exchanger W1 via which heat of reaction from the reactor

can be removed, and which is equipped with a column K1. The column K1 may also comprise an external loop with a heat exchanger W2 via which the excess heat of reaction may be removed. Via the drains 1, 2 and 3 of the column, various reaction products of the reactions occurring in the reactor may be withdrawn.

Example 1:

Into a reactor R1 of the type as shown in Figure 1 (V = 20 m^3, T = 116 °C, p = 2 bar abs.), 4,000 Nm^3/h of Cl_2 and a respective mass flow of ethylene were fed. As the reaction mixture, 18 m^3 of a dichloroethane/catalyst mixture were used. As the catalyst, a sodium chloride modified ferric chloride was used. The reaction selectivity is 99.7 %. A column K1, fitted on top of the reactor, consists of 25 trays and comprises three drains. In total, a reaction heat output of about 11 MW is generated. If in the sump region of the reactor a heat output of 1 MW is removed via heat exchanger W1, a dichloroethane product purity of 99.99 wt% can be achieved.

Example 2:

Into a reactor R1 of the type as shown in Figure 1 (V = 20 m^3, T = 116 °C, p = 2 bar abs.), 4,000 Nm^3/h of Cl_2 and a respective mass flow of ethylene were fed. As the reaction mixture, 18 m^3 of a dichloroethane/catalyst mixture were used. As the catalyst, a sodium chloride modified ferric chloride was used. The reaction selectivity is 99.7 %. The column K1, attached on top, consists of 25 trays and comprises three drains. In total, a reaction heat output of about 11 MW was generated. If in the sump region of the reactor a heat output of 3.5 MV is removed via heat exchanger W1, a dichloroethane product purity of 99.95 wt% can be achieved.

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Továbbfejlesztett eljárás etilén közvetlen klórozása céljából 1,2-diklóretánná

Szabadalmi igénypontok

1. Eljárás 1,2-diklóretán előállítására, melynek során etilént és klórt töltenek a diklóretánnal teli reaktorba, amelyhez desztilláló oszlopot és hőcserélő rendszert csatlakoztatnak; melynek során az etilén és a klór konverziója diklóretánná 80 és 130 °C-on, 0,8 és 5 bar közötti abszolút nyomáson történik, a reakcióelegyet forrásban tartják és a keletkező reakcióhőt részlegesen elvezetik a reakcióelegyből legalább egy hőcserélő segítségével; **azzal jellemezve,** hogy az eljárást olyan készülékkel hajtják végre, amely az alábbiakat tartalmazza:
   a) reaktort; az R1 jelzésű reaktorhoz a P1 jelzésű külső keringtető rendszer csatlakozik, amely tartalmazza a W1 jelzésű hőcserélőt,
   és
   b) a reaktorhoz illesztett desztilláló oszlopot; a K1 jelzésű oszlophoz egy külső keringtető rendszer csatlakozik, amely tartalmazza a W2 jelzésű hőcserélőt.

2. Az 1. igénypont szerinti eljárás **azzal jellemezve**, hogy az ott említett desztilláló oszlop a reaktorból származó reakcióhőt hasznosítja.

3. Az 1. vagy a 2. igénypont szerinti eljárás **azzal jellemezve**, hogy a fent említett reakcióhő elvezetését a reakcióelegyből a fent említett desztilláló oszlop hőigénye szerint szabályozzák.

4. Az 1. igénypont szerinti eljárás **azzal jellemezve**, hogy a reakcióhőt a továbbiakban hasznosítják.

5. Az 1-4 igénypontok bármelyike szerinti eljárás, **azzal jellemezve**, hogy a fent említett hő reakcióelegytől történő elvezetését egy külső hőcserélőhöz történő keringtető csatlakozással oldják meg.

6. Az 5. igénypont szerinti eljárás, **azzal jellemezve**, hogy a reakcióhőt felhasználják más áramló közeg előmelegítésére vagy általánosan alkalmazható keringő fűtőközeg, például melegvíz vagy gőz létrehozására.

7. Az 1.-6. igénypontok bármelyike szerinti eljárás kivitelezésére alkalmas berendezés, **azzal jellemezve**, hogy az említett berendezés az alábbiakat tartalmazza:
   a) az R1 jelzésű reaktort, amelyhez a W1 jelzésű hőcserélőt tartalmazó P1 jelzésű külső keringtető rendszer csatlakozik,
   és
   b) a hozzá illesztett K1 jelzésű desztilláló oszlopot, amelyhez a W2 jelzésű hőcserélőt tartalmazó külső keringtető rendszer csatlakozik.

8. A 7. igénypont szerinti berendezés, **azzal jellemezve**, hogy a reaktorban berendezéseket helyeztek el, és ezek a berendezések előnyösen rögzített terelőlemezek.

9. A 7. vagy a 8. igénypont szerinti berendezés, **azzal jellemezve**, hogy a reakció kiindulási vegyületei külön bemeneteken át adagolhatóak a reaktorba.

10. A 8. igénypont szerinti berendezés, **azzal jellemezve**, hogy az etilént adagolják először az áramlásba az áramlás irányával megegyező irányban.

11. A 7.-9. igénypontok bármelyike szerinti berendezés, **azzal jellemezve**, hogy a fent említett oszlopnak egynél több kivezető nyílása van.

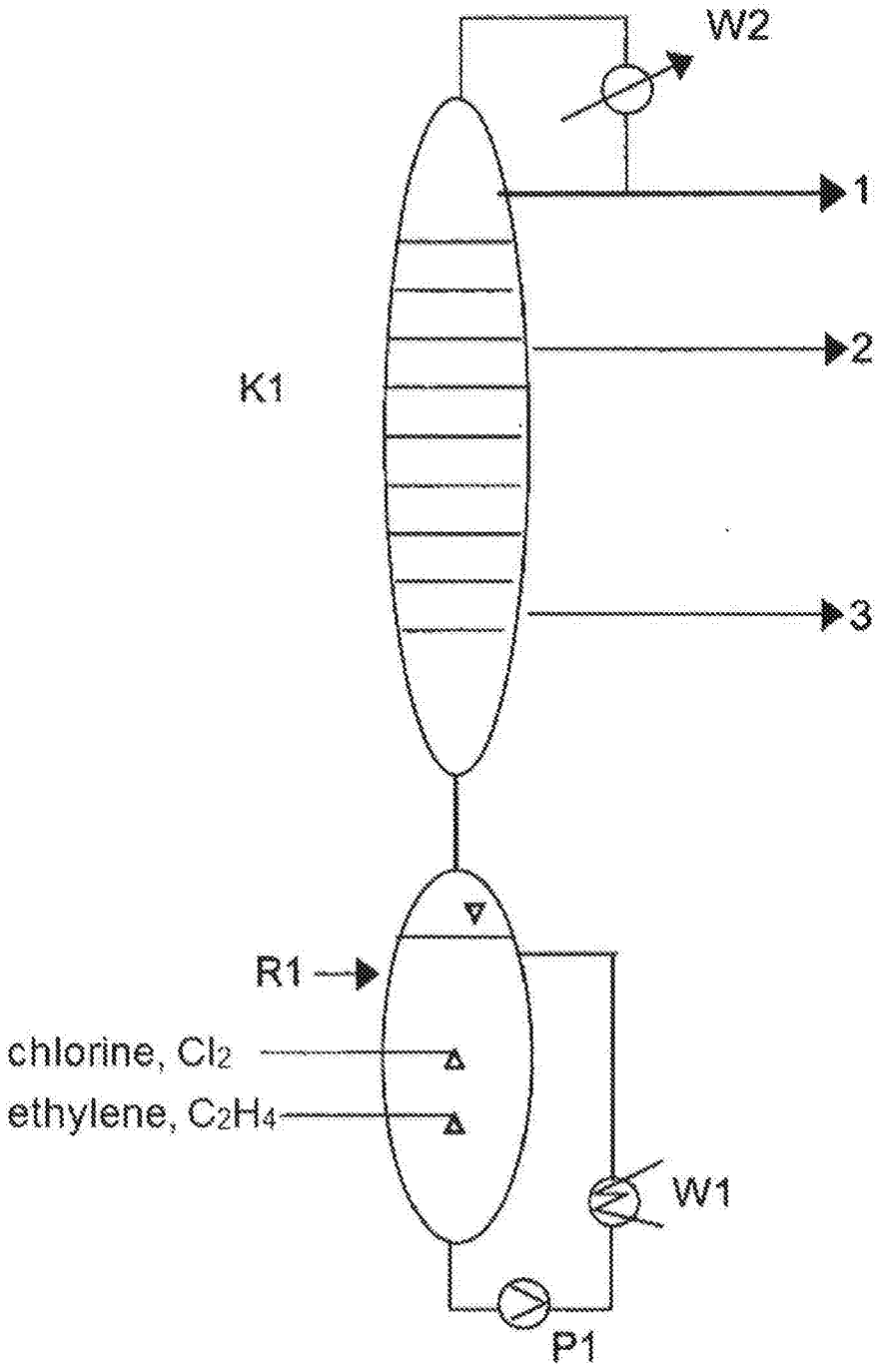

Figure 1