(19) DANMARK

(10) DK/EP 3402774 T3

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: *C 07 C 29/152 (2006.01)* *B 01 J 19/18 (2006.01)* *C 07 C 31/04 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2020-04-27**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2020-02-12**

(86) Europæisk ansøgning nr.: **17712440.1**

(86) Europæisk indleveringsdag: **2017-03-16**

(87) Den europæiske ansøgnings publiceringsdag: **2018-11-21**

(86) International ansøgning nr.: **EP2017056247**

(87) Internationalt publikationsnr.: **WO2017162513**

(30) Prioritet: **2016-03-22 DE 102016204718**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **Siemens Aktiengesellschaft, Werner-von-Siemens-Straße 1, 80333 München, Tyskland**

(72) Opfinder: **BALDAUF, Manfred, Am Kornfeld 52, 91056 Erlangen, Tyskland**
TREMEL, Alexander, Meisenweg 8a, 91096 Möhrendorf, Tyskland
WASSERSCHEID, Peter, Humboldtstr. 15, 91054 Erlangen, Tyskland
ALBERT, Jakob, Ebardstr. 97a, 91054 Erlangen, Tyskland
REICHERT, Jenny, Dorfstraße 2, 97523 Schwanfeld, Tyskland
STARK, Katharina, Paul-Gordan-Straße 19, 91052 Erlangen, Tyskland

(74) Fuldmægtig i Danmark: **Zacco Denmark A/S, Arne Jacobsens Allé 15, 2300 København S, Danmark**

(54) Benævnelse: **Fremgangsmåde med en reaktor med køleindretning**

(56) Fremdragne publikationer:
WO-A1-2015/030578
DE-B- 1 301 524
US-A- 5 712 313
US-A1- 2003 086 853
US-A1- 2007 248 849

The invention relates to a method for operating a reactor according to Claim 1 and use according to Claim 5.

Conversion in chemical reactions is limited by the equilibrium position of the reaction. If the chemical equilibrium of a synthesis reaction lies only partly on the side of the products, a single-stage reaction regime results only in a partial conversion. If, on the other hand, the reaction products are removed from the reactor continuously, there is a continuous conversion of reactants to products within the reactor. For the continuous removal of reaction products it is possible to use sorbents. These sorbents form an additional phase which takes up selectivity products, which are thereby removed from the chemical equilibrium. The sorption phase can be discharged from the reactor together with the product. US-A-5 712 313 discloses a method having a sorbent.

The object of the invention is to provide a method which is suitable for conducting equilibrium-limited reactions using a sorbent and at the same time increase the yield of reaction products relative to the prior art.

The achievement of the object lies in a method having the features of Claim 1.

The not claimed reactor comprises a reaction chamber, where a feed device for reactants, a feed device for a liquid sorbent and also a discharge device for the sorbent are arranged at the reaction chamber. In a lower region of the reaction chamber here there is a sorbent collection zone, and the reactor is distinguished by the fact that there is a cooling device for cooling the sorbent.

The effect of cooling the sorbent is on the one hand that thermal decomposition of the sorbent is prevented, in turn increasing the selection of possible sorbents and allowing the use of more

efficient sorbents in the reaction. On the other hand, the cooling of the sorbent reduces the heating in the reaction chamber as a whole, with positive consequences for the equilibrium conversion of the reaction.

The cooling device is arranged in the region of the sorbent collection zone. This results in effective cooling of the sorbent and in good heat transfer between the cooling device and the liquid sorbent medium.

In turn, the cooling device is arranged so that in one operating state it lies below, or at least partially, a liquid level of the sorbent. As a result of this measure, optimum heat transfer from the cooling device to the sorbent is possible.

A recycling device for recirculating the sorbent is arranged between the discharge device and the feed device. This recycling device is suitable for introducing the sorbent back into the reaction chamber; when the sorbent has already been cooled, this also has positive consequences for the stability during the reaction.

It is useful, furthermore, to arrange a circulating device, more particularly a stirring device, in the sorbent collection zone in order to ensure the exchange of heat between the sorbent and the cooling device.

It is useful, furthermore, to arrange a catalyst space for accommodating a catalyst in the reaction chamber, in order to accelerate the conversion reaction. The catalyst ensures that the reaction proceeds more rapidly, but does not substantially influence the equilibrium state. Reaction products which are at the catalyst surface are absorbed by the sorbent and led from the reaction chamber.

It is useful here if the reaction chamber comprises the catalyst space and a sorption space. Separation of the catalyst material

from the sorbent is useful with many pairings of catalyst and sorbent, since the two substances may influence one another adversely in respect of the reaction.

It is useful again here if the sorption space and the catalyst space are separated from one another by a gas-permeable element. This element in turn is usefully impermeable to liquids or to drips of liquid. In this way, a gaseous reaction product is able to enter the sorption space from the catalyst space more easily, without sorbent present in liquid form being able to pass into the catalyst space. The element may be, for example, a woven fabric, more particularly a metallic woven fabric, or a selective membrane.

It is useful, furthermore, if the reactor comprises a phase separator which is arranged outside the reaction chamber and which serves to carry out separation between sorbent and the reaction product. In this case, this phase separator is in connection with the discharge device of the reactor. In a preferred way, this phase separator is part of the recycling device.

A component of the invention is a method for operating a reactor for implementing equilibrium-limited reactions, having the features of Claim 1.

This method comprises the following steps: first, a number of reaction reactants are introduced into a reaction chamber. Furthermore, a liquid sorbent is likewise introduced into the reaction chamber. The reactants here are passed over a catalyst which is located in the reaction chamber, and are converted therein into reaction products at the catalyst surface until an equilibrium situation occurs. The reaction products are passed from the catalyst surface to the sorbent and are absorbed by said sorbent, after which the sorbent laden with reaction product settles in a sorbent collection zone. A feature of the invention

is that the liquid sorbent is cooled by means of a cooling device in the reaction space.

Here as well there is the advantage, again, that the cooling of the sorbent increases the number of available species; on the other hand, the lowering of the temperature in the reaction chamber has a positive influence on the equilibrium conversion.

In turn it is useful here as well for the sorbent to be cooled by the cooling device in the region of the sorbent collection zone.

It is useful, furthermore, if the sorbent laden with the reaction product is passed off out of the reaction chamber and the reaction product is separated from the sorbent. The sorbent thus unladen can advantageously be recycled by being reintroduced into the reaction chamber.

It is advantageous, furthermore, if the laden sorbent is circulated by a circulation device in the region of the sorbent collection zone, in order to improve exchange with the cooling device.

Further embodiments and further features of the invention are elucidated in more detail with reference to the following figures, in which:

fig. 1 shows a reactor having a reaction chamber and a sorbent collection zone, where the sorbent is cooled in the sorbent collection zone;

fig. 2 shows a reactor analogous to the reactor of fig. 1, where the sorbent is cooled outside the sorbent collection zone.

Fig. 1 depicts a reactor 2, which is embodied in the form of a stirred tank reactor. This reactor 2 comprises a reactant feed device 6 and also a feed device 8 for sorbent 9. In a reaction

chamber 4, reactants 7 and sorbent 9 are introduced. The reaction chamber 4 further comprises a catalyst space 20, which is suitable for accommodating a catalyst 22. The reaction chamber 4 further comprises a sorption space 24, in which the sorbent 9 is located, preferably in droplet form, and settles continuously in the direction of a lower region 11, where there is a sorbent collection zone 12 located.

The text below gives further details of a typical reaction process which takes place in the reactor 2 or in the reaction chamber 4.

The gaseous reactants 7, as already mentioned, are introduced into the reaction chamber 4, and they are passed to the location in the reaction chamber 4 at which the catalyst 20 is present. By the setting of suitable reaction conditions, tailored in each case to the corresponding reaction and/or corresponding reactants, there is an exothermic reaction (giving off heat) of the reactants over the catalyst to form liquid or gaseous reaction products 15. In a gas phase within the reactor, there is an increase in the temperature, with the possible consequence of deactivation mechanisms on the catalyst (boiling or sintering). The gas phase in the reactor here comprises not only gaseous reactants 7 but also possible gaseous reaction products 15. In a reaction arrangement of this kind, the reactants 7 will react maximally until the thermodynamically possible equilibrium conversion, which in certain reactions lies at low values. For example, the reaction of carbon dioxide and hydrogen to give methanol

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \text{eq. 1}$$

is limited thermodynamically by a low equilibrium conversion under typical and economic reaction conditions. The typical reaction conditions for this are a pressure of 75 bar and a temperature of 250°C. As a result of the large amount of heat given off, in other words as a result of the release of energy

during the reaction, the equilibrium conversion is lowered in this reaction, since the reaction temperature rises. It is therefore useful to remove the heat liberated by the reaction of the gas phase from the reaction chamber by means of suitable measures. The measures in question are addressed below.

An appropriate sorbent 9 here is, for example, an aqueous liquid, a heat transfer oil, a salt melt or an ionic liquid which has a high heat capacity but an extremely low vapor pressure. One advantageous mixture for a sorbent is, for example, a mixture of a phosphonium NTf2 IL and an alkali metal or alkaline-earth metal NTf2 salt.

An incomplete listing of suitable ionic liquids is given in table 1.

Table 1: Ionic liquids suitable for sorption (in some cases with admixture of salts)

Ionic liquid
P_{1444} NTf_2
P_{66614} NTf_2
N_{1888} NTf_2
Mixture of P_{1444} NTf_2 and Li NTf_2
Mixture of P_{1444} NTf_2 and Cs NTf_2
Mixture of P_{1444} NTf_2 and Mg $(NTf_2)_2$
Mixture of P_{1444} NTf_2 and Ca $(NTf_2)_2$
P_{1444} $MeSO_4$
P_{1444} Me_2PO_4
EMIM NTf_2
EMIM $MeSO_3$
P_{1444} OTf
P_{2444} Et_2PO_4

The sorbent is able to absorb the heat contained in the gas phase and therefore to lower the temperature of the gas phase. This leads to a homogeneous distribution of temperature in the reaction zone (in the environment of the catalyst) and hence ideally to an isothermic behavior in the reaction chamber 4. This requires effective heat exchange of the gas phase, in other

words, in particular, the phase of the reactants 7, with the absorbent 9.

The catalyst 21 and the sorbent 9 are substances which in certain cases are as far as possible not to come into contact with one another, since such contact may adversely affect their stability and their functionality. For this reason it is useful for the catalyst space 20 to be separated from the sorption space 24 by a gas-permeable element 26. This gas-permeable element 26 may be designed, for example, in the form of a metallic woven fabric or in the form of a membrane which is permeable to the corresponding gas phases. This makes it possible for the generally gaseous reactants 7 to penetrate through the gas-permeable element 26 and react at the catalyst surface to form the reaction products 15. Under the prevailing atmosphere, the reaction products 15 are likewise generally gaseous and they depart the catalyst space 20 through the corresponding element 26. After they have entered through the element 26 into the sorption space 24, they can sorbed by the sorbent 9. The sorbent 9 laden with the reaction products 15 is referred to hereinafter as 9'.

Fig. 1 here shows an embodiment where the sorbent is cooled by a cooling device 13 directly within the reaction chamber 4 in a reactant collection zone 12. This cooling device 13 is designed so that it is arranged below a liquid level 14 of the sorbent collection zone 12. The cooling device 13 is therefore completely immersed in the sorbent in the collection zone 12, leading to highly efficient cooling of the sorbent 9. It is useful, furthermore, to introduce a circulating device 18, in the form of a stirring device 19, for example. The effect of this is that the heated sorbent 9' laden with the reaction products 15 blows continuously around the cooling device 13 in the region of the sorbent collection zone 12, and hence there is optimum heat exchange.

As cooling device 13 it is possible to use heat exchangers disposed in the form of cassettes in the sorbent collection zone 12. In principle, however, other forms of design are also useful;

for example, a cooling device 13 may be integrated directly in a wall of the reaction chamber 4.

The advantage of this embodiment is that the heat can be taken off directly in the reactor 2 or in the reaction chamber 4 and there is no heating in the reaction chamber 4 and therefore no reduced absorption capacity of the sorbent 9 for reaction products 15. A portion of the sorbent 9' laden with the reaction product 15, from the reactant collection zone 12, is subsequently removed from the reaction chamber 4 via a discharge device 10. The laden sorbent 9' is passed into a phase separator 28, in which the sorbent 9 is separated from the product 15. The product 15 is drawn off and collected otherwise. The unladen sorbent 9 is passed back to the feed device 8 for the sorbent 9, by way of a recycling device 16 which comprises a pump 17. The sorbent 9 recycled in this way passes back into the reaction chamber 4 and is ready to receive reaction products 15.

In a further embodiment in accordance with fig. 2, the cooling device 13' is not disposed, as depicted in fig. 1, in the region of the sorbent collection zone 12, but instead in an upper region of the reaction chamber 4. This distinguishes the otherwise identical depictions of fig. 1 and fig. 2. The cooling device 13' arranged at this location promotes the dissolution of reaction products 15 in the sorbent 9 and likewise promotes the condensation of the liquid products 15. As a result of this as well, there is cooling of the reaction chamber 4 and hence of the entire atmospheric environment in the reaction chamber 4, with positive consequences for the reaction conditions and hence for the equilibrium conversion. The reactants 7 are preferably introduced in gaseous form into the reaction chamber 4; alternatively, however, it is also possible for the reactants 7 to be introduced in a condensed phase, in other words in liquid form, into the reaction chamber 4. Reactants 7 here are specifically fed in a liquid or supercritical state at a high fluid density to the reactor 2. Within the reactor, then, in the reaction chamber 4, an evaporation takes place, since under

reaction conditions the reactants or the reactant are or is gaseous. The liquid reactants can be introduced specifically at the location of the release of heat over the catalyst 22. In this case a specific local injection is employed - that is, a corresponding embodiment, not shown here, of the feed device 6 for reactants 7. In the case of the reaction according to equation 1 for the synthesis of methanol, in this case the carbon dioxide reactant would preferably be added in liquid or supercritical form.

Patentkrav

1. Fremgangsmåde til drift af en reaktor til omsætning af ligevægtsbegrænsede reaktioner, omfattende følgende fremgangsmådetrin,
indføring af edukter (7) i et reaktionsrum (4), indføring af et flydende ionisk sorptionsmiddel (9) i reaktionsrummet (4),
hvor edukterne (7) føres til en katalysator (22), der befinder sig i reaktionsrummet (4), og omsættes til reaktionsprodukter (15) på en katalysatoroverflade, indtil der opstår en ligevægtssituation, hvor reaktionsprodukterne (15) når fra katalysatoroverfladen hen til sorptionsmidlet (9) og sorberes af dette, hvorefter sorptionsmidlet (9'), som er ladet med reaktionsprodukterne (15), aflejrer sig i en sorptionsmiddelopsamlingszone, **kendetegnet ved, at** det flydende sorptionsmiddel (9, 9') køles i reaktionsrummet ved hjælp af en køleindretning.

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** sorptionsmidlet (9, 9') køles af køleindretningen (13) i området af sorptionsmiddelopsamlingszonen (12).

3. Fremgangsmåde ifølge krav 1 eller 2, **kendetegnet ved, at** sorptionsmidlet (9'), som er ladet med reaktionsproduktet (15), udledes fra reaktionsrummet (4), og reaktionsproduktet (15) adskilles fra sorptionsmidlet (9'), og det således afladede sorptionsmiddel (9) recirkuleres ved genindføring i reaktionsrummet (4).

4. Fremgangsmåde ifølge et af kravene 1 til 3, **kendetegnet ved, at** det ladede sorptionsmiddel (9') cirkuleres af en cirkulationsindretning (18) i området af sorptionsmiddelsopsamlingszonen (12).

5. Anvendelse af en ionisk væske som sorptionsmiddel i en fremgangsmåde ifølge et af kravene 1 til 4 til kontinuerlig fjernelse af reaktionsprodukter fra en ligevægtsbegrænset reaktion, hvor den ioniske væske omfatter en eller flere bestanddele fra følgende liste:

P_{1444} NTf_2
P_{66614} NTf_2
N_{1888} NTf_2
Blanding fra $P_{1444}NTf_2$ og Li NTf_2
Blanding fra $P_{1444}NTf_2$ og Cs NTf_2
Blanding fra $P_{1444}NTf_2$ og Mg (NTf_2)
Blanding fra $P_{1444}NTf_2$ og Ca (NTf_2)
P_{1444} $MeSO_4$
P_{1444} Me_2PO_4
EMIM NTf_2
EMIM $MeSO_3$
P_{1444} OTf
P_{2444} Et_2PO_4

FIG 1

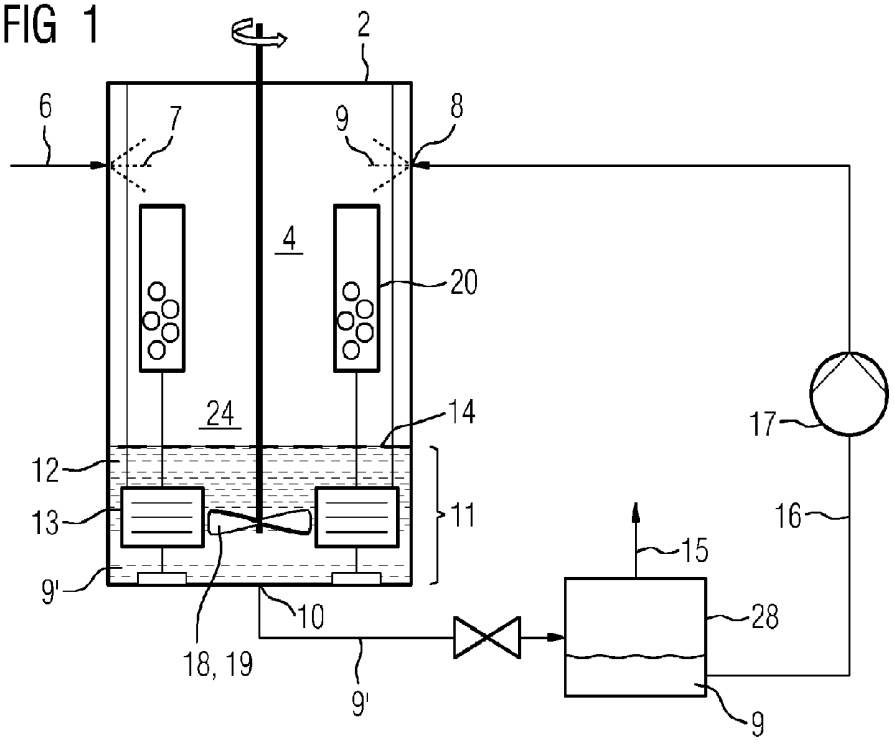
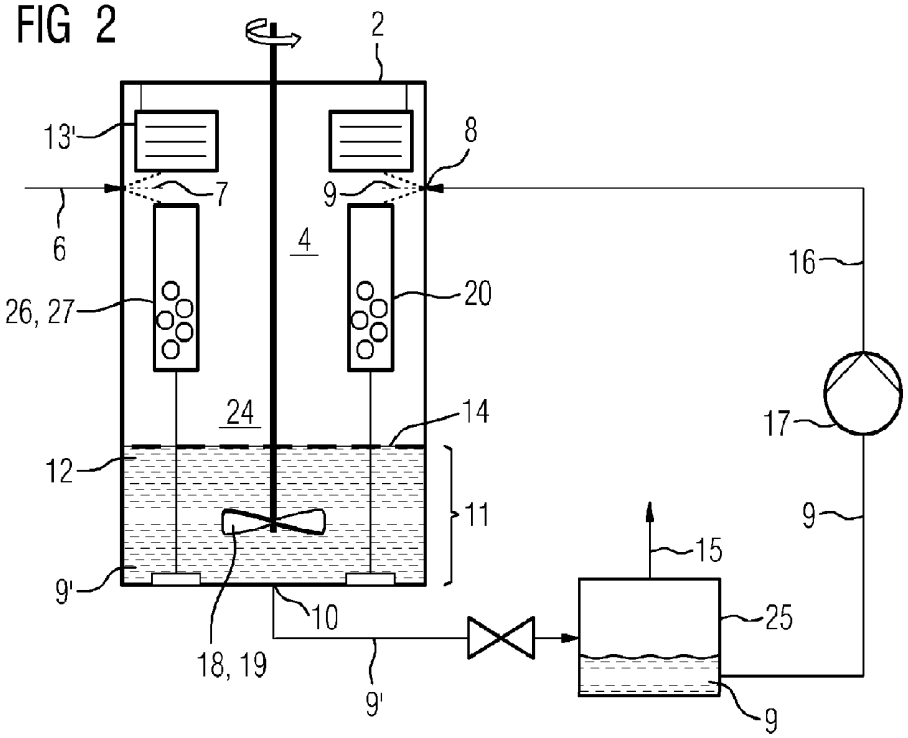

2
6
7
9
8
4
20
24
14
17
12
11
16
13
15
9'
10
28
18, 19
9'
9

FIG 2


2
13'
8
7
9
6
4
16
26, 27
20
17
24
14
12
11
9
15
9'
10
25
18, 19
9'
9