



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 978 501 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

Note: Bibliography reflects the latest situation

(15) Correction information: **Corrected version no 1 (W1 B1)**
Corrections, see page(s) 4, 5

(51) Int Cl.7: **C07C 51/12, C07C 53/08**

(48) Corrigendum issued on:
06.10.2004 Bulletin 2004/41

(45) Date of publication and mention
of the grant of the patent:
10.03.2004 Bulletin 2004/11

(21) Application number: **99113250.7**

(22) Date of filing: **08.07.1999**

(54) **Acetic acid reactive distillation process based on dme/methanol carbonylation**

Reaktiv Destillierungsverfahren zur Herstellung von Essigsäure auf der Basis von DME/Methanol
Carbonylierung

Procédé de production d'acide acétique par distillation reactive basé sur DME/methanol carbonylation

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

(30) Priority: **06.08.1998 US 95457**

(43) Date of publication of application:
09.02.2000 Bulletin 2000/06

(73) Proprietor: **Haldor Topsoe A/S**
2800 Lyngby (DK)

(72) Inventor: **Voss, Bodil**
2830 Virum (DK)

(74) Representative: **Patentanwälte**
Zellentin & Partner
Rubensstrasse 30
67061 Ludwigshafen (DE)

(56) References cited:
EP-A- 0 250 189 **EP-A- 0 497 521**
WO-A-98/22420 **US-A- 4 102 922**

EP 0 978 501 B9

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

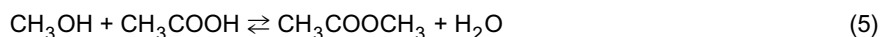
[0001] This invention is directed to a method of producing acetic acid by a reactive distillation process from carbonylation of methanol (MeOH) and/or dimethylether (DME).

[0002] The invention concerns in particular improved production of acetic acid from methanol, DME or a combination of these components over a homogeneous catalyst system contained in a distillation column.

[0003] The catalyst may be any homogeneous carbonylation catalyst which is soluble in the reaction medium.

[0004] The conventional acetic acid synthesis is performed in a homogeneous process, where methanol is carbonylated in a liquid, catalytic medium contained in a stirred reactor. Methanol derivatives such as methyl acetate and dimethyl ether may be applied instead of or in combination with methanol. Carbon monoxide reactant is typically introduced at bottom of the reactor and distributed in the liquid. The catalyst system comprises one or more Group VIII metal compounds, preferably rhodium or iridium and a halide promoter, e.g. methyl iodide (MeI).

[0005] Beside primary reaction (1) other reactions are taking place in the reaction medium. The most predominant are:



[0006] Also small amounts of higher acids, primarily propanoic acid, is synthesized in the process.

[0007] The presence of water is essential to stabilize the catalyst system. So-called stabilizers can be added to the reaction medium in order to reduce the water concentration. A surplus of CO is required to keep the catalyst system activated and unreacted CO gas is purged from the liquid reaction medium at top of the reactor. CO gas (+ inerts and hydrogen synthesized by reaction (2)) stream drives off a fraction of volatile components from the liquid, which is recovered and recycled back to the reaction section.

[0008] The acetic acid product is recovered in a liquid product stream from the reactor and separated by flash off from the catalyst containing reaction medium in a down-stream flash vessel operating at a pressure lower than the reactor pressure, typically at about 0.1 - 0.2 MPa. The liquid from the flash vessel containing the group VIII metal catalyst is recycled to the reactor by means of pumping.

[0009] As acetic acid is the least volatile major compound in the flash medium, the recovery of the acetic acid produced unavoidably leads to the undesired flash off of more volatile components also contained in the flash medium such as water, methyl iodide, methyl acetate, hydrogen iodide and unconverted methanol and dimethyl ether.

[0010] In order to recover these components from the product down stream the reaction section, they are separated in several distillation columns and absorbers and returned to the reaction section.

[0011] The downstream separation process comprises essentially three steps.

1. Primarily methyl iodide and hydrogen iodide are recovered in a light end column and returned to the reactor.
2. Primarily water, methyl acetate, and remaining methyl iodide and hydrogen iodide are recovered in a dehydration column and returned to the reactor.
3. Primarily propanoic acid and a fraction of acetic acid is withdrawn from the bottom of a heavy end column, in which also the product acetic acid is recovered.

[0012] Various overhead gases are separated from methyl iodide in an absorption system.

[0013] In the dehydration column, hydrogen iodide is formed continuously by hydrolysis of methyl iodide (eq. 4)

Eventually, this leads to the formation of a hydrogen iodide/water/acetic acid azeotrope. This azeotrope may be dissociated by addition of small amounts of methanol to the dehydration column.

[0014] Essentially, the resulting component effluents from the acetic acid synthesis and purification sections are unconverted carbon monoxide (+ gases) and the product acetic acid (+ byproducts).

5 [0015] Removal alkanes and alkane-like materials and carbonyl-containing impurities in acetic acid product a stripper column being operated in a reflux manner is disclosed in EP 497,521 A2.

[0016] US 4,102,922 mentions a method for the purification of alkane-containing carbonylation products by distillation of the vaporised products, phase separation of the overhead from the distillation and further distillation of a slipstream of the resulting heavy phase using carbon monoxide as stripping gas.

10 [0017] Reactive distillation of an aqueous effluent from the production of acetic acid with a C1 to C3 alcohol for the removal of the acid is described in WO 98/22420.

[0018] The fact that acetic acid is the least volatile major component in the reaction mixture declines the process economy because of energy consumption and investment in the conventional process layout.

15 [0019] In the process of the present invention the less volatile acetic acid is withdrawn at bottom of the distillation column, while unreacted CO is withdrawn at top of the column. The remaining reactants in the synthesis, or the products at the present chemical equilibria, are remained inside a distillation tower providing simultaneous production and purification of acetic acid product within a distillation column. Accordingly, this invention is a process for the production of acetic acid comprising the steps of

20 (a) carbonylation of methanol, DME or reactive derivatives thereof in a homogenous catalyst solution being active in the carbonylation of methanol, DME or reactive derivatives thereof, in presence of water and a surplus of carbon monoxide;

25 (b) at the same time as (a) collecting the components taking part in present reactions and stripping off mainly unconverted carbon monoxide, hydrogen and inert gases, leaving the remaining components taking part in present reactions; and

30 (c) at the same time as (b) distilling off the acetic acid product from at least part of the remaining components taking part in present reactions, and resupplying the remaining components taking part in present reactions thus reduced in acetic acid to the carbonylation step.

[0020] An advantage of the present invention is that the acetic acid product is efficiently removed from the reaction zone in the reactive distillation process utilizing its low volatility.

[0021] The invention is described in greater detail in the following description.

35 [0022] The span of trays carrying catalyst containing liquid is referred to as reaction zone. The catalyst, which is dissolved in the reaction medium, is prevented from escaping the reaction zone by means of a total pump-around: All the liquid arriving at the bottom of the reaction zone is withdrawn by a recycle stream and returned to a higher tray level.

40 [0023] The tray underneath the reaction zone is fed by liquid main bypass stream from a tray above the reaction zone. An optional by-pass stream being richer in water than the liquid main by pass stream departing from a tray above that of the main bypass stream serves to maintain the desired water concentration in the reaction zone. The water rich by-pass stream is evaporated, such that the water enrichment is performed in the reaction zone and not in the acetic acid rectification part below the reaction zone.

[0024] The condenser at top of the column reduces purge of highly volatile methyl iodide.

45 [0025] The span of trays below the reaction zone to separate acetic acid and higher acids from the remaining components.

[0026] Carbon monoxide and the oxygenate feeds are both introduced below the reaction zone. When the reactants pass the catalyst containing span of trays, they are converted into acetic acid. A surplus of the carbon monoxide serves to maintain an adequate carbon monoxide pressure over the catalyst liquid and further to carrying the vaporized synthesized product (and other components formed of liquid equilibrium reactions) upwardly in the column from the reaction zone. Carbon monoxide is withdrawn at top of the column together with small amounts of essentially methyl iodide. The remaining components are withdrawn in the liquid. main by-pass stream and sent to the lower part of the column. In the lower part of the column an acetic acid product stream is withdrawn together with higher acids, while the components with higher volatility are flowing up through the reaction zone of the column.

50 [0027] From the top of the column a split stream of the unconverted carbon monoxide is optionally sent via a recycle compressor and mixed with a carbon monoxide make-up stream. A carbon monoxide purge stream is purified from methyl iodide in an absorber, and the methyl iodide is returned to the distillation column.

55 [0028] From the bottom of the column, the higher acid containing acetic acid product stream may be sent to a so-called heavy end column as in the conventional layout.

EP 0 978 501 B9 (W1B1)

[0029] The column is operated at 2.4-4.0 MPa (25-40 kg/cm²). The temperature in the column is in the range 150-280EC in the reaction zone and the lower part of the column, whereas in the upper part of the column the operation temperature range is from condenser temperature to about 200EC.

[0030] The molar ratios of the carbon monoxide stream and an oxygenate feed stream may be 1.2:1-2:1. The molar ratio of carbon monoxide stream and the split stream admixture should be at a value providing a partial pressure of carbon monoxide of at least 0.1 MPa (1 kg/cm²), preferably above 0.5 Mpa (5 kg/cm²) in the reaction zone of the column. The molar ratio between the combined carbon monoxide stream and the split stream to the combined streams oxygenate feed stream, the main by-pass stream and the water rich by-pass stream is in the range 0.5:1-3:1. The molar ratio between recycle stream and the combined carbon monoxide stream, the oxygenate stream, main by-pass stream, the water rich by-pass stream and the split stream is in the range 0.5:1-2:1.

[0031] The molar ratio between the main by-pass stream and the acetic acid product stream is 2:1 to 10:1.

[0032] The heat of reaction from the highly exothermic process is removed and e.g. recovered in a steam boiler heated by the recycle stream.

[0033] As an advantage of the present invention, the reactive distillation column replaces several operation units of the conventional layout, such as stirred carbonylation reactor, flasher, light end column, dehydration column, LP absorber, pumps and pipes.

[0034] As another advantage of the present invention the catalyst solution contrary to the known processes is not subjected to a flash vaporization. The flash operation, as carried out in the conventional process, leads to a considerable reduction in CO partial pressure rendering the catalyst subject to inactivation and precipitation as described e.g. in EP 55,618, 161,874 and 250,189.

[0035] The flash-evaporation of the conventional layout may also lead to mist formation in the flash vessel, whereby small catalyst containing droplets, which are carried over to the distillation system down-stream. Thus, the process of the present invention eliminates the loss of catalyst associated with flash vaporization.

[0036] It is essential to the process economy to keep the rhodium catalyst loss at a minimum, as rhodium is costly.

[0037] A further advantage of the present invention is that hydrogen iodide will not accumulate in the column, because the oxygenate feed stream is introduced to the distillation column at a stage eliminating the critical water limit of the column at which the hydrogen iodide is normally accumulated, due to the dissociation induced azeotrope. By introducing the oxygenate feed stream at a number of trays below the reaction zone, hydrogen iodide is efficiently converted into methyl iodide in the presence of methanol.

[0038] If the demand on water concentration is low, the internal liquid flow and carbon monoxide flow rates are relatively low.

[0039] If the demand on the water concentration is high, a large CO recycle is required, and a secondary bypass stream richer in water than the water rich by-pass stream after evaporation is introduced beneficially. The number of trays below the reaction zone must be increased accordingly in order to obtain proper separation.

[0040] At high internal flow rates, a net heat supply of about 0.8 Gcal/MT acetic acid is required (which is similar to the equivalent range of the conventional acetic acid synthesis), while at low internal flow rates, the net heat requirements are considerably reduced or even slightly negative. **[deletion(s)]**

Claims

1. A process for the production of acetic acid comprising the steps of

(a) carbonylation of methanol, DME or reactive derivatives thereof in a homogenous catalyst solution being active in the carbonylation of methanol, DME or reactive derivatives thereof, in presence of water and a surplus of carbon monoxide;

(b) at the same time as (a) collecting the components taking part in present reactions and stripping off mainly unconverted carbon monoxide, hydrogen and inert gases, leaving the remaining components taking part in present reactions; and

(c) at the same time as (b) distilling off the acetic acid product from at least part of the remaining components taking part in present reactions, and resupplying the remaining components taking part in present reactions thus reduced in acetic acid to the carbonylation step.

2. A process as recited in claim 1, wherein the simultaneous steps (b) and (c) are carried out at the same pressure level as (a).

3. A process as recited in claim 2, wherein the simultaneous steps are conducted within a distillation column.
4. A process as recited in claim 1, wherein the catalyst system comprises at least one element of Group VIII metal compounds.

5

Patentansprüche

1. Verfahren zur Herstellung von Essigsäure, enthaltend die Schritte

10

a) Carbonylierung von Methanol, DME oder deren reaktiven Derivaten in einer homogenen Katalysatorlösung, welche bei der Carbonylierung von Methanol, ME oder deren Derivaten aktiv ist, in Gegenwart von Wasser und einem Überschuss von Kohlenmonoxid;

15

b) zu a) gleichzeitiges Sammeln der bei den vorliegenden Reaktionen teilnehmenden Komponenten und Abstreifen von hauptsächlich nicht umgesetztem Kohlenmonoxid, Wasserstoff und Inertgasen unter Belassen der übrigen an den vorliegenden Reaktionen teilnehmenden Komponenten; und

20

c) gleichzeitig zu b) Abdestillieren des Essigsäureprodukts aus wenigstens einem Teil der verbleibenden, an den vorliegenden Reaktionen teilnehmenden Komponenten und Wiederezuführen der verbleibenden, an der vorliegenden Reaktion teilnehmenden, auf diese Weise reduzierten Komponenten in Essigsäure zum Carbonylierungsschritt.

2. Verfahren zur Herstellung von Essigsäure nach Anspruch 1 **dadurch gekennzeichnet, dass** die simultanen Schritte b) und c) im selben Druckniveau durchgeführt werden, wie a).

25

3. Verfahren zur Herstellung von Essigsäure nach Anspruch 2 **dadurch gekennzeichnet, dass** die simultanen Schritte in einer Destillationskolonne durchgeführt werden.

30

4. Verfahren zur Herstellung von Essigsäure nach Anspruch 1 **dadurch gekennzeichnet, dass** das Katalysatorsystem Metallverbindungen von mindestens einem Element der Größe VIII umfasst.

Revendications

1. Procédé de production d'acide acétique comprenant les étapes :

35

(a) la carbonylation du méthanol, de DME ou des dérivés réactifs de ceux-ci dans une solution de catalyseur homogène, étant active dans la carbonylation du méthanol, de DME ou des dérivés réactifs de ceux-ci, en présence d'eau et d'un surplus de monoxyde de carbone;

40

(b) en même temps que (a), le recueil des composants participant aux présentes réactions et l'élimination par entraînement principalement du monoxyde de carbone non converti, de l'hydrogène et de gaz inertes en laissant participer les composants restants aux présentes réactions; et

45

(c) en même temps que (b), le retrait par distillation du produit acide acétique d'au moins une partie des composants restants participant aux présentes réactions et la ré-alimentation de l'étape de carbonylation en les composants restants participant aux présentes réactions, ainsi réduits en acide acétique.

2. Procédé selon la revendication 1, dans lequel les étapes simultanées (b) et (c) sont effectuées au même niveau de pression que dans (a).

50

3. Procédé selon la revendication 2, dans lequel les étapes simultanées sont conduites dans une colonne de distillation.

55

4. Procédé selon la revendication 1, dans lequel le système catalytique comprend au moins un élément parmi les composés métalliques du Groupe VIII.