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(54) Title: IMPROVED GAS STRIPPING PROCESS FOR THE RECOVERY OF SOLVENTS FROM FERMENTATION BROTHS

(57) Abstract: Process for the production of solvents comprising a fermentation step and a gas stripping step under isothermal conditions.



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## IMPROVED GAS STRIPPING PROCESS FOR THE RECOVERY OF SOLVENTS FROM FERMENTATION BROTHS

The present invention relates to a process for the recovery of a solvent, in particular  
5 butanol, from a fermentation broth comprising an isothermal gas stripping step.

The synthesis of solvents such as alcohols by fermentation provides a viable  
alternative to chemical processes using petroleum products which will have to be replaced  
in the near future. The production of solvents by microbial fermentation has many  
advantages. For example, the production of ethanol, isopropanol, acetone, 1-butanol,  
10 isobutanol, 1,3-propanediol and 1,2-propanediol by fermentation are well known. The raw  
starting material in the fermentation medium can be glycerol, glucose, sucrose, starch or  
any other cheap sugar source, such as agricultural waste.

In particular, the synthesis of 1-butanol by fermentation has for example been  
described in US 6,358,717, US 5,192,673 and US 4,568,643. Efforts are currently made to  
15 increase the efficiency of 1-butanol production by fermentation, which is limited by 1-  
butanol toxicity to the host organism. Thus, one major problem encountered during the  
production of 1-butanol is the limitation of the fermentation productivity by alcohol  
inhibition.

As a consequence, various methods have been described to remove fermentation  
20 products and in particular alcohols from the fermentation broth in a continuous way, so  
that micro-organism activity is not affected in the culture medium. Liquid-liquid extraction  
(US 4,865,973 and US 4,628,116), gas stripping (US 4,703,007, US 2005/0089979,  
WO 2007/149370A1) adsorption (US 4,450,294) and membrane separation (US  
5,755,967) have been described for recovery of volatile fermentation products.

25 Ennis *et al.* (Biotechnology letters, vol. 8, No. 10, pages 725-730, 1986) describe  
continuous product recovery by *in-situ* gas stripping/condensation during solvent  
production. Production and purification of butanol are carried out in an integrated batch-  
fermentor-gas stripping apparatus.

US 4,703,007 describes recovery of low concentration volatile metabolites from  
30 fermentation broth by gas stripping. The solvents are directly recovered from the liquid  
media during continuous culture of the microorganism. The stripping gas supplied to the  
system is usually of large volume.

US 2005/0089979 also describes a continuous process for the production of solvents by fermentation comprising removing solvents directly from the fermentor by passing a flow of stripping gas through the culture.

Therefore, when solvents are produced by fermentation, gas stripping is in most cases directly carried out in the fermentor e.g. by means of adding gas through spargers. However, this set up lacks separation efficiency and huge amounts of water must be evaporated to recover the desired amount of solvent. Another major drawback with these methods is that both fermentation conditions and gas stripping conditions have to be tightly controlled in the same reactor. Further, the process, described in both US 4,703, 007 and US 2005/0089979, requires a high gas flow rate which afterwards makes the recovery of the solvent from the stripping gas both difficult and costly.

WO 2007/149370 is directed to a process for making isooctenes from dry 1-butanol. The 1-butanol reactant for the process is derived from fermentation broth. Various methods are cited for separation of 1-butanol from clarified fermentation broth including gas stripping. Detailed conditions for separation of solvents by gas stripping are however not described. Qureshi and Maddox (1991) describe an integrated system for continuous production and product recovery of solvents (acetone-butanol-ethanol). The fermentation reactor effluent is stripped of the solvents in a separate stripping unit using nitrogen gas and is recycled to the fermentation reactor. However, the gas stripper is a continuous stirred vessel and this type of reactor does not allow an efficient recovery of the solvent with a high yield.

JP 62029990 describes purification of ethanol by distilling a specific ethanol extracting gas directly under supercritical conditions. This extraction under supercritical conditions carried out at 150bar is completely different from gas stripping.

EP 0282474 describes production and purification of solvents produced by fermentation. Gas stripping is used for the recovery of the solvent but detailed conditions are not described.

WO 2009/079362 is directed to methods for controlling butanol concentration in a fermentation broth. A portion of the fermentation broth is continuously removed followed by stripping and absorption. Thus, gas stripping is given as an example, but detailed conditions are not described.

In the petrochemical industry, gas stripping is a separation technique which is commonly used to remove traces of organic pollutants or traces of water from mixtures of

interest. Thus, the stripped compound is of low value in most cases and is not recovered. Steam stripping processes for recovery of water-insoluble organic compounds are the only stripping applications dedicated to the recovery of valuable chemicals from a liquid mixture. In most of these cases, the concentration of the pollutant to be removed is very  
5 low in the liquid treated, so that there isn't any particular specification neither on operating temperature, nor on gas flow rate.

Thus, recovery of solvents/alcohols by gas stripping from a fermentation broth has to overcome unusual challenges.

One of the major challenges is the high solvent flow rate to be removed from the  
10 liquid phase (fermentation broth), thus requiring a high flow rate of stripping gas. Because a large volume of stripping gas is used, removal of the valuable solvent from the enriched stripping gas makes the whole process not cost effective. This removal step is in most cases achieved by condensation at a low temperature. Some specific process settings improve the condensation efficiency such as for example elevating the gas pressure before  
15 the condensation unit. However, in the case of solvents produced by fermentation the need to remove valuable solvents from large volumes of fermentation broth and therefore also from large volumes of enriched stripping gas renders the whole process inefficient and expensive.

The gas stripping unit may be a reactor providing for mixing of the liquid  
20 fermentation broth and of the stripping gas with an agitator such as described by Qureshi and Maddox (1991). This system may only require a small volume of stripping gas but the yield of solvent removed from the liquid is very insufficient under such conditions. On the other hand, the volume flow rate of stripping gas can be increased to improve the yield of solvent removed, but the amount of water evaporated is tremendous.

25 The present invention provides for a gas stripping in a gas stripping unit providing at least two theoretical stages of separation. The liquid fermentation broth is fed at the top of the unit, and the inert gas is counter-currently circulated to strip volatiles, including the solvent, from the liquid.

30 However, in such a system a major challenge is the need to operate at temperatures which are both relatively low to be compatible with fermentation, and sufficient to allow evaporation of the solvents. When contacting an inert gas and a liquid in an adiabatic system, the partial evaporation of the liquid leads to a temperature drop of the mixture compensating the heat of vaporization of the stripped product. This temperature drop leads

to a less efficient removal of solvent from the fermentation broth by stripping and to attain the comparable yields increased amounts of stripping gas have to be used. Thus, some authors have suggested increasing the temperature of the liquid at the inlet of the stripping unit, to compensate for the temperature drop. However, the increase of temperature at the inlet of the gas stripping unit doesn't completely prevent the temperature drop of the system. Moreover, such methods are conflicting with the fermentation conditions required to obtain satisfying solvent production. Indeed, to reach efficient stripping, the inlet temperature would have to be raised to levels which are not compatible with fermentation relying on live microorganisms.

10 The present invention relates to a process in which fermentation and gas stripping are carried out in separate units. In several sections of the stripping unit heat duty is applied to slightly elevate the temperature of the fermentation broth, thus ensuring isothermal or nearly isothermal conditions during gas stripping.

A major advantage of this process is that the gas stripping can be carried out at the fermentation temperature, thus without preliminary clarification of the fermentation broth. After the gas stripping step, the solvent-depleted fermentation broth can be recycled to the fermentor. The process and apparatus allow for continuous fermentation and stripping in which the concentration of solvent is efficiently regulated in the fermentation broth. Thus, the solvent concentration in the fermentation broth is kept sufficiently low to prevent inhibition of the activity of the micro-organisms. The recycling of solvent-depleted fermentation broth and the regulation of solvent concentration in the fermentor are both efficient ways to improve the solvent productivity by fermentation. Advantageously, the isothermal gas stripping of the present invention increases the solvent-to-carbohydrate yield of the fermentation step, and microorganism activity is not affected by the gas stripping.

By compensating the temperature drop due to partial liquid evaporation, the gas flow rate required to recover a given quantity of solvent is dramatically reduced. Thus, in the process of the present invention reduced flow rates of stripping gas are required to remove valuable solvent from a fermentation broth. In the methods according to the invention, the use of an isothermal gas stripping column greatly improves the solvent removal yield of the gas stripping step.

The solvent recovered in the gas stripping step may be further purified by known processes, such as distillation, to produce pure solvent.

SUMMARY OF THE INVENTION

The present invention relates to a process for the production of solvents comprising:

- 5 a. Obtaining by fermentation in a fermentor a fermentation broth containing a liquid culture media, a biomass and a solvent produced by said biomass,
- b. Transferring said fermentation broth from the fermentor to a gas stripping unit,
- 10 c. Removing the solvent from said fermentation broth by gas stripping in a gas stripping unit ensuring a flow of fermentation broth and a counter flow of stripping gas and providing at least two theoretical stages of separation under isothermal conditions to obtain a solvent-enriched stripping gas and a solvent-depleted fermentation broth,
- d. Recovering the solvent from said solvent enriched-stripping gas.

15 Preferably, the fermentation broth may be clarified prior to transferring said fermentation broth to the gas stripping unit.

In preferred embodiments, the stripping gas is carbon dioxide.

Advantageously, the gas stripping under isothermal conditions is carried out a temperature comprised between 15°C and 80°C, preferably between 15°C and 60°C and even more preferably between 30° C and 40°C. In most preferred embodiments,  
20 fermentation and gas stripping are carried out at the same temperature comprised between 15°C and 80°C, preferably between 15°C and 60°C and even more preferably between 30°C and 40°C.

Preferably, the gas stripping is carried out in gas stripping unit comprising a gas stripping column equipped with trays and/or packings providing at least two theoretical  
25 stages of separation.

Preferably, the gas stripping under isothermal conditions is carried out with a mass ratio of stripping gas flow at the inlet of the gas stripping unit to fermentation broth flow at the inlet of the gas stripping unit comprised between 0.5 and 5, preferably between 1 and 3, and even more preferably between 1.5 and 2.5.

30 After gas stripping, the solvent is typically recovered from the solvent enriched stripping gas by condensation. Advantageously, the solvent enriched stripping gas is compressed before condensation.

After recovery of the solvent, the solvent depleted fermentation broth is preferably recycled to the fermentor.

In preferred embodiments, the process of the present invention comprises further purification of the solvent by distillation.

5 In preferred embodiments, the invention relates to the production of butanol, in particular 1-butanol. During fermentation, the biomass advantageously comprises a micro-organism selected from *Clostridium acetobutylicum* and *Escherichia coli* for the production of 1-butanol.

The invention also relates to an apparatus for the production of solvents by  
10 continuous fermentation and gas stripping comprising:

- a) A fermentor containing a fermentation broth consisting of a liquid culture media, a biomass and a solvent produced by said biomass,
- b) A gas stripping unit having means ensuring a flow of fermentation broth and a counter flow of stripping gas, means providing at least two theoretical stages of  
15 separation and means to operate under isothermal conditions,
- c) Means for continuously circulating said fermentation broth between the fermentor and the gas stripping unit.

In preferred embodiments, the gas stripping unit comprises a gas stripping column equipped with trays and/or packings providing at least two theoretical stages of separation.

20 Preferably, the apparatus also comprises a condensation unit.

The apparatus may further comprise at least one distillation column for the further purification of the solvent.

## FIGURES

25

Figure 1: Improved process to produce solvents, by associating a fermentation step with an improved gas stripping step. (1) Stripping unit (without preliminary clarification step), (2) Fermentation process, (3) Final purification process, (4) Solvent condensation, (5) Fermentation broth clarification.

30 Figure 2: Improved process to produce solvents, by associating a fermentation step with an improved gas stripping step. (1) Stripping unit (with preliminary clarification step), (2) Fermentation process, (3) Final purification process, (4) Solvent condensation, (5) Fermentation broth clarification.

Figure 3: Final purification process, in the case where solvent to be purified is 1-butanol. (1) First Distillation step, (2) First decantation step (3) Second distillation step (4) Second decantation step, (5) Third Distillation step.

Figure 4: Improved final purification process, in the case where solvent to be purified is 1-butanol. (1) First distillation step, (2) First decantation step, (3) Second distillation step, (4) Liquid Withdrawal, (5) Second decantation step.

### DETAILED DESCRIPTION OF THE INVENTION

10           The present invention relates to the production of solvents by fermentation and more particularly to the increase of solvent productivity in a fermentative production route. The present invention is directed to a continuous process, associating a fermentation step with a gas stripping step carried out in isothermal conditions, to produce a solvent-rich or alcohol-rich mixture. After stripping, the solvent-rich or alcohol-rich mixture is treated by  
15 known processes, e.g. distillation, evaporation, liquid-liquid extraction or any appropriate technique, to obtain pure solvent.

          “Solvent” refers to any organic molecule obtained by fermentation starting from carbohydrates, glycerol, or any other raw material. Advantageously, agricultural wastes are used as cheap sugar sources for fermentation processes.

20           Preferred solvents produced by the process of the present invention are for example butanol (1-butanol, 2-butanol, isobutanol), ethanol, iso-propanol and acetone.

          Preferably, the solvent of the present invention is an alcohol. “Alcohol” means a molecule with at least one alcohol function. Preferred alcohols produced by the process of the present invention are 1-butanol, 2-butanol, ethanol, iso-propanol. Even more  
25 preferably, the alcohol produced by the methods of the present invention is 1- butanol.

          In a preferred embodiment, the invention relates to an improved production process of butanol from a fermentation broth comprising a source of carbohydrates. Such fermentation leads to the production of by-products such as acetone, ethanol and acids. Improvements of the fermentative production of butanol, e.g. by using metabolically  
30 engineered micro-organisms, are described in WO 2008/052973.

          In the present application, fermentation means the conversion of a carbohydrate into a solvent or an alcohol. Solvent is produced in a fermentation broth comprising a liquid culture media containing a carbohydrate source and a micro-organism. The raw

material, for example a mixture of carbohydrates, is converted by suitable micro-organisms to solvents. Generally, the temperature is kept constant between 20°C and 80°C during fermentation. Preferably, temperature is kept constant between 30°C and 40°C, depending on the micro-organism used for fermentation.

5           Production of solvents by fermentation may be carried out with any suitable microorganisms or mixtures thereof. Preferably, the microorganism is selected in the group consisting of *Clostridium acetobutylicum*, *Clostridium beijerinckii*, *Clostridium saccharoperbutylacetonicum*, *Clostridium butylicum*, *Clostridium butyricum*, *Clostridium perfringens*, *Clostridium tetani*, *Clostridium sporogenes*, *Clostridium thermocellum*,  
10 *Clostridium saccharolyticum* (now *Thermoanaerobacter saccharolyticum*), *Clostridium thermosulfurogenes* (now *Thermoanaerobacter thermosulfurigenes*), *Clostridium thermohydrosulfuricum* (now *Thermoanaerobacter ethanolicus*), *Escherichia coli* and *Klebsiella pneumoniae*. Most preferably, the micro-organism producing the solvent is *C. acetobutylicum* or *Escherichia coli*.

15           In the present application, “biomass” includes the micro-organisms but also any large molecules such as proteins and cell debris for example which are produced by said micro-organisms. During fermentation, fermentation broth comprises liquid culture media, biomass and solvent produced by the micro-organisms.

          The fermentation broth obtained contains a low concentration of solvent and  
20 solvent concentration has to be maintained at a low level in order to avoid inhibition of the micro-organism. The solvent therefore has to be removed from the fermentation broth continuously to ensure efficient production of the solvent.

          In the present invention, the fermentation broth is preferably continuously transferred from the fermentor to a gas stripping unit for the removal of the solvent from  
25 the fermentation broth.

          Advantageously, the solvent-depleted fermentation broth is also continuously recycled to the fermentor.

          Any means for transferring the fermentation broth from the fermentor to the gas stripping unit may be used.

30           In some embodiments, the fermentation broth is clarified prior to transferring said fermentation broth to the gas stripping unit. This step consists in eliminating insoluble elements, most notably the biomass containing micro-organisms, proteins and suspended particles. Preferably, all molecules heavier than 200 Da are eliminated. This clarification of

the fermentation broth is for example carried out by filtration or by centrifugation. “Filtering” preferentially means a membrane separation method. Advantageously, filtration consists of microfiltration and/or ultrafiltration and/or nanofiltration steps. “Centrifugating” preferentially means a separation method based on gravitational force.

5 Centrifugation could be achieved in continuous or discontinuous way. In preferred embodiments, the biomass containing the micro-organisms used for fermentation is recycled to the fermentor.

More generally, any desired pre-treatment of the fermentation broth may be performed prior to the gas stripping step.

10 “Fermentor” means any apparatus, device or fermentation reactor that maintains optimal conditions for the growth of micro-organisms and for the production of solvents by said micro-organisms.

Removal of the solvent from the fermentation broth is carried out by gas stripping under isothermal conditions.

15 “Gas stripping” means a process in which the solvent-containing liquid fermentation broth is contacted with an inert gas to remove volatile components including the solvent produced by the micro-organism from the liquid fermentation broth. Solvents are selectively evaporated from the fermentation broth.

“Gas stripping unit” means any apparatus, device, tower, pipe or column ensuring a  
20 flow of liquid fermentation broth and a counter-flow of gas that strips volatiles from the liquid and providing at least two, three, four or at least five theoretical stages of separation. A “theoretical stage” describes any device that ensures separation of the fed mixture in such a manner that the thermodynamic equilibrium is reached between the two phases produced. In the case of stripping, the thermodynamic equilibrium (i.e. Henry’s Law)  
25 indicates that the higher the solvent concentration in the liquid, the higher the solvent concentration in the gas. Thus, an objective of the invention is to maximise the concentration of solvent in the liquid which is in equilibrium with the gaseous outlet of the stripping device. A way to achieve that goal is to increase the efficiency of the stripping device, i.e. its number of theoretical stages.

30 In a stirred vessel, as suggested by Qureshi and Maddox (1991), the maximum efficiency is only a single theoretical stage: thus, the concentration of solvent in the gaseous product is directly linked to the residual concentration in the liquid. The

consequence is the impossibility to reach both low residual concentration in the liquid (i.e., high yield) and high concentration in the gaseous product (i.e., low operating costs).

In preferred embodiments, the gas stripping unit comprises a column equipped with packing, trays, or any other means known to the skilled technician ensuring maximal  
5 efficiency of the gas-liquid separation in at least two, three, four or at least five theoretical different stages. Typically, in such a column, fermentation broth will flow from the top down over numerous trays while the stripping gas is injected at the bottom and removed at the top.

Any appropriate inert gas may be used as stripping gas in the present invention.  
10 Preferably, the stripping gas is selected from carbon dioxide, nitrogen, air, hydrogen, or a mixture thereof. In a preferred embodiment, the stripping gas is carbon dioxide. In another embodiment, the inert gas used for stripping is produced by the fermentation itself. In this case, carbon dioxide, hydrogen, or mixtures thereof produced during fermentation are for example used for the stripping step.

15 In the methods of the present invention conventional gas stripping conditions may be used. In particular, the pressure in the gas stripping unit is comprised between 1.5 bar and 0.1 bar. Typically the pressure in the gas stripping unit is about 1 bar.

In the present invention, the gas stripping step is carried out under isothermal conditions. Further, the gas stripping step is carried out in a gas stripping unit which is  
20 separate from the fermentor.

In the present invention the gas stripping unit provides for at least two, three, four or at least five stages of separation which increases the efficiency and yield of the solvent recovery. The drawback of this system is the partial evaporation of the water contained in the fermentation broth leading to a temperature drop and to a temperature gradient in the  
25 gas stripping unit. In the present invention, this difficulty is overcome by the use of a gas stripping unit having means to operate under isothermal conditions.

“Isothermal” refers to a gas stripping operation carried out at a nearly constant temperature. The temperature of the gas stripping unit or of the fermentation broth is maintained or kept constant by any means within five degrees, preferably, within two  
30 degrees, above and under a given goal value.

“Means to operate under isothermal conditions” are known to the skilled person and include for example internal heat exchangers, heating jackets, recirculation of liquid on external heat exchangers, steam feeding, or any combination of these devices.

In a preferred embodiment, the temperature of the fermentation broth in the gas stripping unit is maintained constant at a temperature comprised between 15°C and 80°C, preferably between 15°C and 60°C and even more preferably between 30° C and 40°C.

Advantageously, the temperature in the gas stripping unit is kept constant within  
5 values which are compatible with micro-organism activity. Thus, the fermentation broth may be transferred directly and continuously to the gas stripping unit without the requirement of a preliminary clarification step. The solvent-depleted fermentation broth is also easily recycled to the fermentor. Preferably, the solvent-depleted fermentation broth is mixed with a carbohydrate-rich mixture, thus providing a fresh feed for the fermentation  
10 step. The solvent concentration in the solvent-depleted fermentation broth is well below the inhibition level. Therefore, the micro-organisms activity is not affected. Recycling of the solvent-depleted fermentation broth recycling significantly increases solvent productivity of the fermentation process.

As fermentation and gas stripping are carried out in different units, each reaction  
15 can be controlled independently and therefore more efficiently. Further, the gas stripping unit includes trays, packings and any other means which improve separation of the volatiles (solvents) from the fermentation broth by providing at least two, three, four or at least five theoretical stages for separation of the liquid fermentation broth and the volatiles including the solvent. Continuous fermentation and gas stripping are made possible by  
20 continuous removal of solvents and recycling of the fermentation broth.

In some embodiments, the temperatures of the fermentation broth in the gas stripping unit, is higher in than the temperature of the fermentation broth in the fermentor. Preferably, the temperature in the gas stripping unit is within temperature ranges that microorganisms can withstand.

25 In another embodiment of the invention, the temperature in the gas stripping unit is kept constant at a value higher than the maximum temperature compatible with the microorganism. In this embodiment, the fermentation broth is clarified before being treated by gas stripping, and the microorganisms are recycled to the fermentor.

A crucial advantage of the process according to the invention is that the amount of  
30 stripping gas required to recover the solvent from the fermentation broth is dramatically reduced.

Preferably, gas stripping under isothermal conditions is carried out with a mass ratio of stripping gas flow at the inlet of the gas stripping unit to fermentation broth flow at

the inlet of the gas stripping unit comprised between 0.5, 1, 2, 3, 4 and 5, preferably between 1 and 3, and even more preferably between 1.5 and 2.5.

This gas stripping step yields a solvent-enriched stripping gas and a solvent-depleted fermentation broth. After this step, most of the solvent has been removed from the  
5 fermentation broth.

Surprisingly, thanks to the isothermal stripping conditions the volume of solvent-enriched stripping gas is significantly reduced which enables efficient recovery of the solvent.

The process and apparatus of the present invention provide for a high yield in the  
10 recovery of the solvent in a cost efficient manner as the volume of the solvent enriched stripping gas is reduced.

Any appropriate method may be used to recover the solvent from the stripping gas. A preferred method is condensation in which the solvents are condensed from a gaseous state to a liquid state. Any appropriate condenser or condensation unit may be used in the  
15 methods of the present invention. Water and solvents contained in the gaseous product of the stripping step are condensed. In preferred embodiments, the solvent enriched stripping gas is compressed before condensation. Once the solvent-rich stripping gas has been compressed, condensation may be carried out at higher temperatures. Condensation yields a solvent-depleted gaseous product and a solvent-rich condensate.

20 The solvent-rich condensate produced by the condensation step may be treated by distillation or by any other process known by to the skilled person, to obtain further purified solvent.

Advantageously, the solvent is further purified by distillation. In the case of 1-butanol purification, the distillation process may comprise three steps. The feed is treated  
25 by a first distillation step to obtain a 1-butanol rich mixture at the top of the column, and a 1-butanol-depleted aqueous product at the bottom of the column. After a sufficient settling time, the mixture obtained at the top provides an aqueous phase and a butanol-rich organic phase. The aqueous phase is recycled to the top of the first distillation step, and the organic phase is sent to the second distillation step. Light impurities, e.g. acetone and ethanol, are  
30 removed at the top of the second distillation step. After a sufficient settling time, the bottom product of the second distillation step provides an aqueous phase and a butanol-rich organic phase. The aqueous phase is recycled to the top of the first distillation step, and the organic phase is sent to the third distillation step. The third distillation step is to remove

the residual water at the top of the column, by distilling the water-1-butanol heteroazeotrope. The azeotropic mixture is recycled to the first distillation step, while pure 1-Butanol is obtained at the bottom of the column. The operating pressure of the three distillation steps are chosen between 0.1 bar and 2 bar, preferably between 0.9 bar and 1.2  
5 bar.

Any distillation column, device or unit may be used for the purification of the solvent.

Advantageously, the distillation process described above can be improved to give a two-steps distillation process, as described in FR2549043.

10 Remaining impurities may be further removed by ion exchange or adsorption but these techniques are used as polishing techniques to reach an even higher final quality. Fouling of the ion exchange resins or of the adsorbent solid is reduced because salts and heavy impurities have been removed beforehand.

In the methods of the present invention, activated charcoal or other solid adsorbents  
15 like ion-exchange resins may be used to remove colour-forming or odour-forming impurities from the purified alcohol. This purification step may be performed at any moment in the process of the present invention.

The present invention provides a stable continuous process, which leads to purified solvent or alcohol, particularly 1-butanol, with a better productivity and yield than the  
20 existing methods.

The present invention also concerns an apparatus for the production of solvents comprising:

- a fermentor containing a fermentation broth consisting of a liquid culture media, a biomass and a solvent produced by said biomass,
- 25 - a gas stripping apparatus having means ensuring a flow of fermentation broth and a counter flow of stripping gas, means providing at least two theoretical stages of separation and means to operate under isothermal conditions,
- means for circulating said fermentation broth between the fermentor and the gas stripping apparatus.

30 Preferably, the solvent is butanol.

Preferably, the gas stripping unit comprises a gas stripping column equipped with trays providing at least two, three, four or at least five theoretical stages of separation of the liquid fermentation broth from the volatiles including the solvent.

The apparatus may further comprise a condensation unit for recovering the solvent from the stripping gas.

The apparatus for production and recovery of solvents combining fermentation and gas stripping may also comprise one or more distillation columns or distillation units for  
5 further purification of the solvent.

The process and apparatus of the present invention are further exemplified by figures 1-4.

The whole process, associating a stripping column (1) with a fermentation step (2), is described in figure 1. Solvent-rich fermentation broth is continuously withdrawn from  
10 the fermenter (2) and then split between the stripping unit (1) and the final purification process (3). As described in the above invention, the final purification process usually consist in distillation process, as described in figures 3 and 4. A part of the fermentation broth is counter-currently contacted with an inert gas flow in the stripping unit (1), to recover solvents in the gas phase and to produce a solvent-depleted fermentation broth. In  
15 that configuration the fermentation broth is not clarified before being treated in the stripping unit (1), which supposes that the temperature in the gas stripping unit is within temperature ranges that microorganisms can withstand. The solvent-depleted fermentation broth is recycled upstream of the fermenter (2) and mixed with a carbohydrate-rich feed, thus providing a new feed of the fermentation process (2). The solvent-rich gaseous  
20 product of the stripping unit (1) is compressed and solvents are condensed to obtain a solvent-rich condensate (4) and a solvent-depleted gaseous mixture. The solvent-depleted gaseous mixture is recycled upstream of the stripping unit (1) bottom feed and mixed with a fresh gas make-up, thus providing the gaseous feed of the stripping unit (1). The solvent-rich condensate is fed to the final purification process (3). The fermentation broth which is  
25 not treated by the stripping unit (1) is clarified, e.g. by filtration (5) and fed to the final purification process (3). The final purification process allows producing pure solvent, from clarified fermentation broth (5) and solvent-rich condensate (4).

Figure 2 describes the same process that Figure 1, except that the whole fermentation broth withdrawn from fermenter (2) is clarified, e.g. by filtration (5), whether  
30 being treated in the stripping unit (1) or fed to the final purification process (3). In that configuration, the temperature in the gas stripping unit can be higher than the maximum temperature withstood by the microorganisms.

Figure 3 describes a typical purification process, consisting in three distillation steps. A butanol solution is fed to the first distillation step (1), to produce butanol-rich vapors at the top, and a butanol-depleted stream at the bottom. 1-butanol is not fully miscible in water, thus the mixture obtained by condensation of the butanol-rich vapors is fed to the first decantation step (2). The decantation step produce a water-rich mixture, which is recycled to the first distillation step (1) and an organic-rich mixture, which is fed to the second distillation step (3). The second distillation step (3) produces a top product enriched in light impurities and a bottom product enriched in butanol. Thanks to the removal of light organic impurities, a water-rich mixture may be produced by a second decantation step (4). That water-rich mixture is recycled to the first distillation step (1). Butanol-rich mixture obtained from decantation step (4) is fed to the third distillation step (5), to produce pure solvent at the bottom, and to recycle remaining water and lights impurities from the top to the second decantation step (2).

Figure 4 describes an improved purification process, consisting in two distillation steps. The first distillation step (1) and the first decantation step (2) are common with the process described in figure 3. The organic-rich mixture produced by decantation step (2) is fed to an improved second distillation step (3). A liquid mixture is withdrawn (4) from the distillation column (3) and fed to a decanter (5) to produce a water-rich mixture and an organic rich mixture. The water-rich mixture is recycled to the first distillation unit (1) and the organic rich mixture is sent back to the second distillation unit. Thus, a pure butanol stream is obtained at the bottom of the column, and the light impurities are removed at the top of the column.

## EXAMPLES

25

These examples, while indicating preferred embodiments of the key step of the described invention, i.e. a gas stripping step carried out in isothermal conditions, are given by way of illustration only.

### 30 Example 1: Gas stripping operation carried out near adiabatic conditions

An aqueous solution of 1-butanol is used as a raw material for the experiment, the weight fraction of 1-butanol in the feed is 1w %. The gas stripping column used has a inner diameter of 35 mm, and a packed height of 1m50. It is equipped with a double jacket, in

which water can be circulated at a known temperature. That heating system is not used for that first experiment, thus ensuring that the gas stripping operation is carried out near adiabatic conditions.

The liquid feed flow rate at the top of the column is about 1.2 liter per hour. Carbon dioxide is used as the stripping gas carrier. The gaseous feed flow rate is 15 liter per minute (at 25°C and 1 bar). Gas and liquid feeds are counter-currently contacted in the column: the separation efficiency is maximized by using suitable packing in the column. Rashig rings made of borosilicate glass are used for that experiment. The gas stripping of the liquid solution leads to evaporation of at least a part of water and solvents.

10 Table 1 : Example 1 – Operating conditions

Parameters	
Liquid feed flow (kg/h)	1.23
Butanol weight fraction in the feed	0.99%w
Gas feed flow (l/min)	15
Resulting Gas/Liquid mass ratio (calculated)	1.35
Liquid feed pre-heating (°C)	45
Temperature in the column	See table below
Bath temperature for jacket heating (°C)	Not used

The table below presents the evolution of the temperature in the column and the butanol content of the liquid bottom product.

15 Table 2 : Example 1 - Results

Time (min)	Butanol weight fraction in the bottom product	Temperature at the top of the column °C	Température at the middle of the column, °C
18	0.70%	34.3	25.1
33	0.62%	34.3	24.9
47	0.62%	34.4	24.8
62	0.62%	33.9	25.1
80	0.62%	34.0	25.2

The temperature in the middle of the column shown that in adiabatic conditions, equilibrium temperature in the column rapidly drops near the ambient temperature. The butanol weight fraction of the bottom liquid product is decreased by 38%. The bottom liquid product mean flow rate is 1.06 kg/h: the yield of butanol removal by gas stripping is

5 46%.

Example 2: Gas stripping operation carried out at 35°C, near isothermal conditions

The system described in Example 1 is used. Water at a regulated temperature of 35°C is circulated through the double jacket of the stripping column, thus ensuring

10 isothermal conditions.

The liquid feed flow rate at the top of the column is about 1.2 liter per hour. Carbon dioxide is used as the stripping gas carrier. The gaseous feed flow rate is 15 liter per minute (at 25°C and 1 bar).

Table 3 : Example 2 – Operating conditions

Parameters	
Liquid feed flow (kg/h)	1.19
Butanol weight fraction in the feed	0.94%w
Gas feed flow (l/min)	15
Resulting Gas/Liquid mass ratio (calculated)	1.4
Liquid feed pre-heating (°C)	45
Temperature in the column	See table below
Bath temperature for jacket heating (°C)	37

15

The table below presents the evolution of the temperature in the column and the butanol content of the liquid bottom product.

Table 4 : Example 2 - Results

Time (min)	Butanol weight fraction in the bottom product, w%	Temperature at the top of the column °C	Temperature at the middle of the column, °C	Temperature at the bottom of the column, °C
51	0.40%	36.1	34.7	38.2
69	0.45%	36.1	34.6	37.4
88	0.45%	36.3	34.6	37.6
92	0.46%	36.2	34.5	37.5

The temperature in the column is efficiently maintained near the goal value of 35°C. The consequence is a greater yield of butanol removal yield from the bottom liquid product : the weight fraction of the bottom liquid product is decreased by 55%. The bottom liquid product mean flow rate is 1.044 kg/h : the yield of butanol removal by gas stripping is 58%. That operation has been carried in the same operating conditions than the operation described in the example 1, excepted that the heating double-jacket has been used. The result is an increase of 25% of the Butanol removal from the liquid feed.

10 Example 3: Gas stripping operation carried out at 45°C, near isothermal conditions

The system described in Example 2 is used. The temperature of the thermo-regulated is set to 50°C to ensure a nearly constant operating temperature of 45°C in the column.

The liquid feed flow rate at the top of the column is about 1.2 liter per hour. Carbon dioxide is used as the stripping gas carrier. The gaseous feed flow rate is 15 liter per minute (at 25°C and 1 bar).

Table 5 : Example 3 – Operating conditions

Parameters	
Liquid feed flow (kg/h)	1.20
Butanol weight fraction in the feed	0.97%w
Gas feed flow (l/min)	15
Resulting Gas/Liquid mass ratio (calculated)	1.39
Liquid feed pre-heating (°C)	45
Temperature in the column	See table below
Bath temperature for jacket heating (°C)	50

The table below presents the evolution of the temperature in the column and the butanol content of the liquid bottom product.

Table 6 : Example 3 - Results

Time (min)	Butanol weight fraction in the bottom product, w%	Temperature at the top of the column °C	Température at the middle of the column, °C	Température at the bottom of the column, °C
15.5	0.13%	41.6	47.0	45.8
31.3	0.14%	42.0	46.7	46.0
49	0.14%	42.3	46.3	46.0
63.5	0.14%	42.3	46.5	46.0
80.5	0.14%	42.9	46.3	45.9
92.75	0.13%	42.0	46.3	45.8

The temperature in the column is efficiently maintained near the goal value of 45°C. The consequence is a greater yield of butanol removal yield from the bottom liquid product :  
 5 the weight fraction of the bottom liquid product is decreased by 55%. The bottom liquid product mean flow rate is 1.038 kg/h : the yield of butanol removal by gas stripping is 87%. Thus, a temperature increase of 10°C leads to a butanol removal yield increase of 50%.

10

Example 4: Gas stripping operation carried out at 55°C, near isothermal conditions, on a fermentation broth

The system described in Example 3 is used. The operating temperature in the  
 15 column is set to 55°C. A fermentation broth containing about 10 g/l of 1-Butanol is used. That fermentation broth was microfiltered on 0.22 µm hollow-fibers membrane before being treated by stripping.

The liquid feed flow rate at the top of the column is about 1.6 liter per hour. Carbon  
 20 dioxide is used as the stripping gas carrier. The gaseous feed flow rate is 15 liter per minute (at 25°C and 1 bar).

Table 7 : Example 4 – Operating conditions

Parameters	
Liquid feed flow (kg/h)	1.64
Butanol weight fraction in the feed	0.97%w
Gas feed flow (l/min)	15
Resulting Gas/Liquid mass ratio (calculated)	1
Liquid feed pre-heating (°C)	45
Temperature in the column	See table below
Bath temperature for jacket heating (°C)	60

The temperature in the column is efficiently maintained near the goal value of 55°C. The  
5 butanol weight fraction in the bottom liquid product is 0.15w %. The bottom liquid product  
mean flow rate is 1.42 kg/h : the yield of butanol removal by gas stripping is 86%.

Thus, the increase of the operating temperature leads to the same Butanol removal yield  
than in the example 3, where the gaseous to liquid feeds flow rates ratio was far lower.  
10 That example shows the efficiency of the gas stripping operation for the butanol removal  
from a clarified fermentation broth.

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CLAIMS

1. A process for the production of butanol comprising:
  - 5 a. Obtaining by fermentation in a fermentor a fermentation broth containing a liquid culture media, a biomass and butanol produced by said biomass,
  - b. Transferring said fermentation broth from the fermentor to a gas stripping unit,
  - 10 c. Removing butanol from said fermentation broth by gas stripping in a gas stripping unit ensuring a flow of fermentation broth and a counter flow of stripping gas and providing at least two stages of separation under isothermal conditions to obtain a butanol-enriched stripping gas and a butanol-depleted fermentation broth,
  - d. Recovering butanol from said solvent enriched-stripping gas.
- 15 2. A process for the production of butanol according to claim 1 wherein the fermentation broth is clarified prior to transferring said fermentation broth to the gas stripping unit.
3. A process for the production of butanol according to anyone of claims 1-2, wherein the stripping gas is carbon dioxide.
- 20 4. A process for the production of butanol according to anyone of claims 1-3, wherein said gas stripping under isothermal conditions is carried out at a temperature comprised between 15°C and 60°C.
- 25 5. A process for the production of butanol according to anyone of claims 1-4, wherein fermentation and gas stripping are carried out at the same temperature comprised between 30° C and 40°C.
- 30 6. A process for the production of butanol according to anyone of claims 1-5, wherein the gas stripping is carried out in gas stripping unit comprising a gas stripping column equipped with trays providing at least two stages of separation.

7. A process for the production of butanol according to anyone of claims 1-6, wherein said gas stripping under isothermal conditions is carried out with a mass ratio of stripping gas flow at the inlet of the gas stripping unit to fermentation broth flow at the inlet of the gas stripping unit comprised between 1 and 3.
- 5
8. A process for the production of butanol according to anyone of claims 1-7, wherein butanol is recovered from the butanol enriched stripping gas by condensation.
9. A process for the production of butanol according to anyone of claims 1-8, wherein the
- 10 butanol depleted fermentation broth is recycled to the fermentor.
10. A process for the production of butanol according to anyone of claims 1-9 comprising further purification of the solvent by distillation.
- 15 11. A process for the production of butanol according to anyone of claims 1-10 wherein the biomass comprises a micro-organism selected from *Clostridium acetobutylicum* and *Escherichia coli* for the production of 1-butanol.
12. An apparatus for the production of butanol by continuous fermentation and gas
- 20 stripping comprising:
- a. A fermentor containing a fermentation broth consisting of a liquid culture media, a biomass and butanol produced by said biomass,
  - b. A gas stripping unit having means ensuring a flow of fermentation broth and a counter flow of stripping gas, means providing at least two stages of
  - 25 separation and means to operate under isothermal conditions,
  - c. Means for continuously circulating said fermentation broth between the fermentor and the gas stripping unit.
13. An apparatus for the production of butanol according to claim 12 wherein the gas
- 30 stripping unit comprises a gas stripping column equipped with trays providing at least two stages of separation.

14. An apparatus for the production of butanol according to anyone of claims 12-13 comprising a condensation unit.
  15. An apparatus for the production of butanol according to anyone of claims 12-14
- 5 comprising a distillation unit.

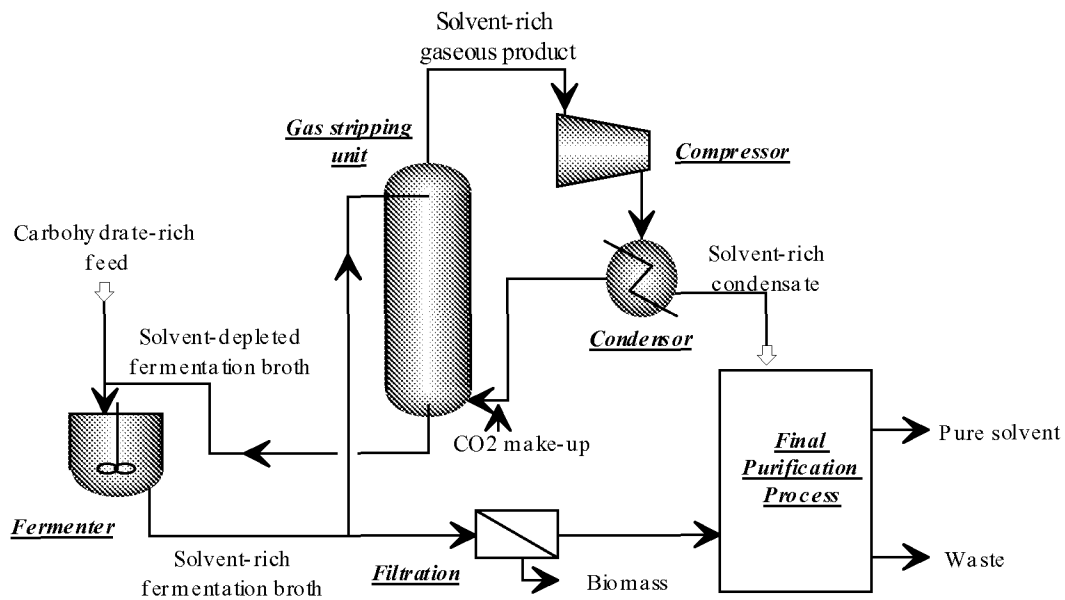


Fig.1

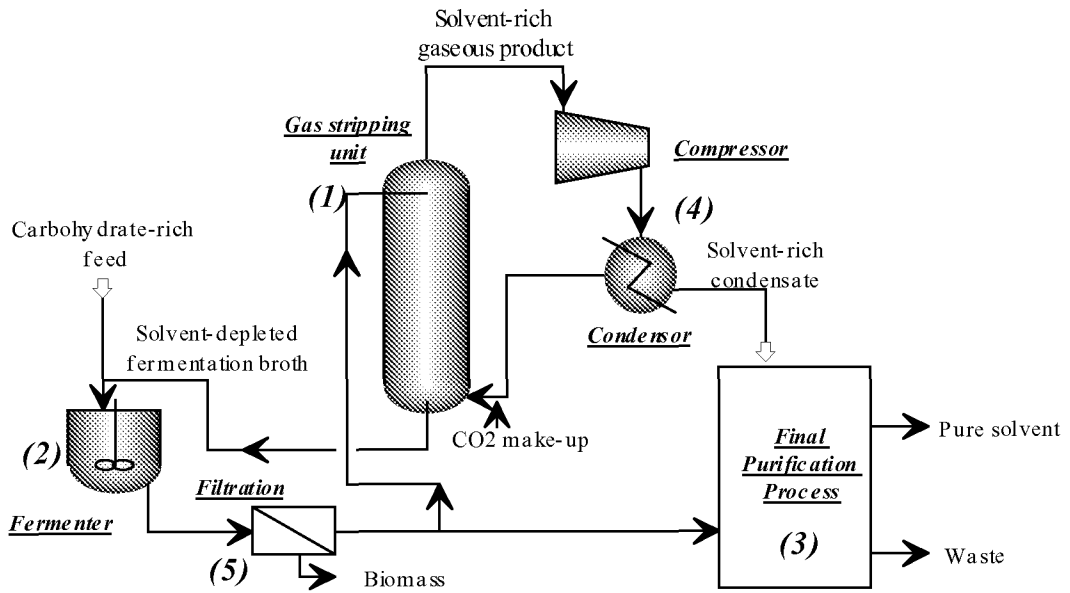


Fig.2

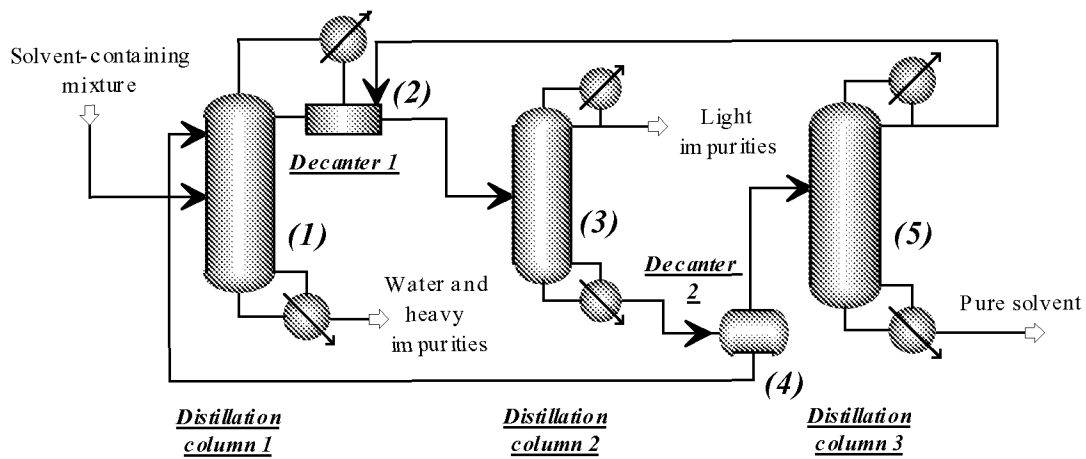


Fig.3

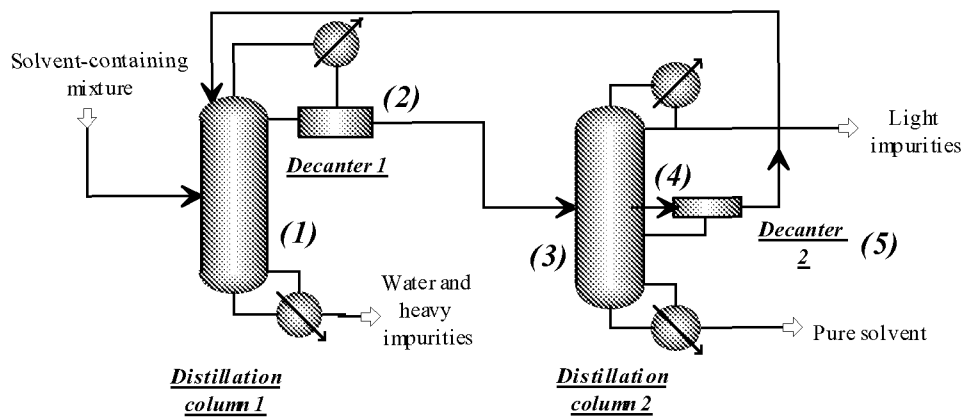


Fig.4