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(54) Title: A METHOD FOR THE REMOVAL OF A GAS FROM A PROCESS GAS STREAM BY MEANS OF LIQUID CRYSTALS

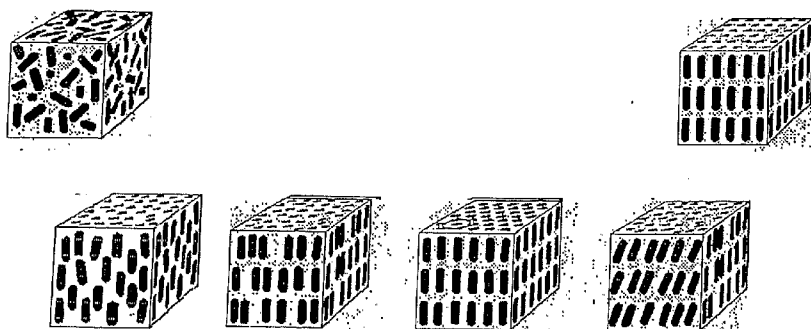


Fig. 1

(57) Abstract: The present invention relates to a method for the removal of a component from a process gas stream using liquid crystals as solvent for the gas to be removed. The present invention applies a phase change from the isotropic state to the nematic state, wherein the solubility of the gas to be removed is drastically reduced, such that the component to be removed desorbs from the solvent. The phase change is realized by lowering the temperature of the solvent or by raising the pressure. According to the present invention, components that can be removed include among others: CO₂, H₂S, H₂O, etc.

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A method for the removal of a gas from a process gas stream by means of liquid crystals

The present invention relates to a method for the removal of a gas from a process gas stream by contacting the same with an absorption solvent for the removal of gas, followed by desorption of the gas to be removed.

5 Solvents for the removal of process stream substances are used on a large scale in various separation processes, such as extraction processes, absorption processes, extractive distillation, crystallisation processes, etc. This involves the dissolutions of the substances to be removed in the solvent,
10 also referred to as "loading" the solvent. The solvent containing the dissolved substances is subsequently treated, whereby the dissolved substances are removed from the solvent and the solvent generated herewith, which clearly contains fewer dissolved substances, can be reused.

15 A considerable drawback of such a process is that the cycle of loading the solvent and regenerating is associated with significant energy consumption, with the ensuing high operating expenses and capital expenditure.

20 The object of the present invention is to provide a method, in which the above-mentioned drawbacks are effectively eliminated, so as to render the cycles of loading and regenerating efficient and economical.

To this end the present invention provides a method for the removal of a gas from a process gas stream by contacting the
25 same with a solvent for the gas to be removed, followed by desorption of the gas to be removed, characterized in that as solvent liquid crystals are used.

According to the present method, isotropic liquid crystals are used, wherein after absorption of the gas to be
30 removed under the influence of heat and/of pressure a phase-change from the isotropic to the nematic condition is realized, wherein the solubility of the gas to be removed is drastically reduced such that the gas to be removed desorbs for the most part, leaving a solvent that is sufficiently free of gas to be
35 removed, and that can be reused.

In accordance with the prior art conventional solvents are used. Generally, absorption processes are conducted in such a way that for the removal of substances a solvent is contacted with a raw gas stream. The substances that are soluble in the solvent will dissolve. The solvent is then regenerated in a desorption step, also referred to as stripping. Desorption involves the consumption of a significant amount of energy for the reduction of the partial pressure of the dissolved substances. This is often realized by using steam as stripping gas, with the temperature being raised and the partial pressure of the dissolved substances in the steam phase being lowered. This is necessary for the regeneration of the solvent.

It should be noted, that the present invention can be applied in a large number of the processes mentioned above. However, for illustration purposes the principles of the present invention are explained with regard to an absorption/desorption process, to which the invention is in no way limited. Absorption processes are, for example, used for the removal of acid gas components from a gas stream. The solvent that is used for the absorption is usually regenerated and reused, creating a cycle of absorption and regeneration (desorption).

Surprisingly it was shown that when the solvent used for the separation process, i.e. the absorption and regeneration process, comprises of liquid crystals in the isotropic phase the dissolved substances, usually gases, could be removed with much higher energy efficiency than according to the prior art described above. According to the invention loading, that is to say absorption of the soluble substances, occurs in the solvent while this is in the above-mentioned isotropic phase. By causing the isotropic phase of the loading solvent to change to a nematic phase the solubility of the dissolved substances is considerably reduced, resulting in an effective desorption of the dissolved substances so as to realize efficient regeneration of the solvent.

Attention is drawn to the fact that de phase change between isotropic and nematic (generally referred to as mesomorphic) phases of the liquid crystalline solvents drastically changes the solubility of the dissolved substances. According to the invention, it is this phase change that is exploited, in the sense that loading (absorption) takes place in the isotropic

phase, while regeneration occurs (or is promoted) through the phase change to the nematic phase, with the result that the solubility of the dissolved substances is significantly reduced.

Although the principles are explained with respect to
5 absorption/desorption processes, it does not mean that the invention should be limited to these. Said principles may also be applied to extraction processes, extractive distillation, reactive extractive processes, etc.

As to the solvents forming the liquid crystalline
10 phase, these may be ordinary solvents, i.e. solvents that do not have a permanent molecular charge, or iogenic liquids (ionic liquid crystals).

To illustrate the present invention one takes, for example, the absorption of component A from a stream of A + B
15 using a liquid crystalline solvent C. The absorption of A in the solvent C takes place in, for example, a phase contacting device (e.g. a staged absorption column). The solvent phase is then at least partly isotropic. After altering the temperature and/or the pressure, the solvent phase undergoes a phase change to a
20 liquid crystalline phase (e.g. a nematic phase). As a consequence, the solubility of A is drastically reduced, resulting in the regeneration of the solvent.

As mentioned before, an important aspect of the present invention is the application of liquid crystals as solvent for
25 the solutes to be removed.

In recent years, liquid crystals have increasingly been the subject of research activities, so far mainly directed at optical properties and related products such as, for example LCDs.

30 The general concept of liquid crystals is further clarified below.

Liquid crystals are substances with a molecular order between crystals and liquids. In a particular temperature range the molecules exhibit an imperfect long-range order of molecular
35 orientation. However, if the temperature is raised to above a sharp phase change temperature, the molecular order is disrupted, bringing about an isotropic state. This phase change drastically alters the thermodynamic behaviour in relation to other components, comparable to a solubility switch. Despite

intensive and wide interdisciplinary research directed at liquid crystals, their application as process solvents is a new field.

The inventors have devoted extensive research to the exploration and facilitation of the applicability of liquid crystals as separating means, i.e. as extraction media, absorption liquids and as separation-promoting agents. An important objective is, for example, to demonstrate that liquid crystals are suitable for use as absorbing (scrubbing) solvents in gas washing processes, in connection with the recovery of carbon dioxide from waste gasses.

It should be noted that with relatively large molecular structures the number of liquid crystals seems to be innumerable. This, in turn, opens the possibility of optimizing the design of molecules for a particular purpose. The observation that liquid crystals are very well controllable low/non-volatile (green) solvents that may be rendered suitable for particular applications, has so far not been developed in the chemical engineering community, nor has it as yet been mentioned in scientific publications. As background regarding liquid crystals it may be stated that substance can exist in the solid, liquid or gaseous state.

In the solid state, molecules are ordered positionally as well as orientationally, while in liquids the molecular position as well as the molecular orientation is random over a number of (molecular) diameters. Some substances may assume a fourth state, namely the liquid crystalline state, in which a directional order is assumed instead of no (or only a partial) positional order. The liquid crystalline phase lies between the solid and the liquid phase.

Figure 1 is an illustration of molecular order in a liquid phase, in various liquid crystalline phases and in a solid crystalline phase. In Figure 1 the two cubes in the top row from left to right represent liquid (isotropic) and crystal, respectively. The four cubes in the bottom row from left to right represent: nematic (LC), smectic A (LC), smectic B (LC), and smectic C (LC), respectively.

Notably, the application of liquid crystals is very diverse; examples of this are liquid crystal thermometers, optical imaging, non-destructive mechanical tests of materials under stress, visualization of radio frequency waves in wave guides,

medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured, erasable optical discs, full-colour electronic slides for computer-aided drawings (CAD), light modulators for colour electronic
5 imaging, stationary phase in chromatography, etc. It appears that most applications of liquid crystals benefit from the direction of molecular ordering, which is controllable via electric or magnetic fields; or vice versa, that the changes in ordering caused by variations in pressure, temperature, etc. are
10 detected by way of electric or magnetic fields or optically.

As mentioned above, the present invention is based on a sharp phase change between the isotropic state of liquid crystals and the nematic state, at which phase change it was surprisingly shown that the solubility of the substances in the
15 liquid crystals diminishes drastically, with the result that the dissolved substances desorb and disappear almost completely from the solvent.

An example of this is CO₂. If CO₂ needs to be removed from a stream of natural gas (or hydrogen in the case of a fuel
20 cell application), liquid crystals may be used as an absorbing solvent in an absorption column at a temperature T^{abs} , wherein the absorption capacity for carbon dioxide is X^{abs} . If the liquid crystals are cooled by a few degrees Kelvin, the liquid crystal-line phase undergoes a phase change to a nematic phase, and a
25 phase separation is observed. Surprisingly, the solubility of carbon dioxide in a nematic liquid is shown to drop sharply to X^{des} .

The thus regenerated liquid crystals can be fed back to the absorption step with little effort.

30 The nematic-isotropic change thus serves as a switch in CO₂-solubility, which can be employed by small-range temperature variations of the mixture. Compared with the conventional absorption/desorption concepts, the present approach may be said to be very advantageous and elegant because no phase change of
35 the liquid takes place involving substantial energy-intensive temperature variations that range from approximately 30 to 80 K.

According to the invention, the above-mentioned phase change from the isotropic to the nematic state is attained by lowering the temperature or raising the pressure. An approximate
40 temperature-variation of typically 20 K is desired.

The present invention is suitable for the efficient removal of CO₂, H₂S, etc. from process gas streams.

Solvents, that is to say liquid crystals that are suitable for dissolving the solute, i.e. CO₂, H₂S, etc. are trans-4-(4-pentylcyclohexyl)-benzonitrile or their derivatives. It is observed, that when CO₂ is removed from high-pressure gas streams, for example streams occurring with Syngas production (H₂, CO, H₂O, CO₂) or with fuel cell applications where reforming gas streams are treated, the pressure of the feed streams are typically in the range of 20-60 bars. When using a liquid crystalline solvent for the absorption of carbon dioxide in a traditional absorption column, wherein the solubility of the other gas components is considerably lower, the temperature of the absorption column is 50-150 °C. When using PCH5 (4-(trans-4-pentylcyclohexyl)-benzonitrile) as solvent, absorption occurs at approximately 50 °C. This is above the nematic-isotropic phase change temperature, wherein $T^{NI} = (54.6 - x) \text{ }^{\circ}\text{C}$, wherein x denotes the pressure of the transition temperature due to carbon dioxide ($x \approx 5 - 20 \text{ }^{\circ}\text{C}$), depending on the partial pressure of the carbon dioxide.

It should be noted, that use may also be made of the phase change between two mesomorphic phases, such as nematic and smectic, but also between an isotropic phase and, for example, a smectic phase.

The invention will now be further explained by way of the Examples 1 - 3.

Example 1: Removal of CO₂ from a natural gas stream

A CO₂-containing natural gas stream is contacted with a liquid crystal solvent in an absorption step. The natural gas stream may comprise 10 mol % of CO₂ and has a temperature of approximately 40 °C. The solubility of CO₂ in isotropic PCH-5 is approximately 5% by mass. A fourfold mass of liquid crystals is contacted with the natural gas stream for the absorption of CO₂. The product gas comprises residual amounts of CO₂, depending on the purity of the regenerated liquid crystal solvent and the mass transport specifications of the apparatus. The residual amount of CO₂ is estimated at approximately 1 molpercent. The regeneration of the liquid crystal solvent occurs by lowering the temperature to approximately 25 °C so as to achieve a

nematic phase, and by using nitrogen as stripping gas. After absorption, the regenerated solvent is again recycled, so as to obtain an absorption/desorption cycle.

5 Example 2: Removal of CO₂ from a natural gas stream

A process stream derived from a water stream "reforming" process after a water-gas shift is treated with liquid crystals to remove the carbon dioxide from the process stream (absorption). The process stream has a pressure of approximately 14
10 bars. Depending on the raw materials used in the generation of the water stream, the process stream may contain 30 molpercent of CO₂. In order to scavenge carbon dioxide from the process stream, a counter stream is contacted with a liquid crystalline substance in a nematic phase. The carbon dioxide dissolves in
15 the nematic liquid in an amount of approximately 5% by mass. The process continues as described in Example 1.

Example 3: Removal of H₂S from the process stream

In Example 1 a CO₂-polluted natural gas field was described. In a similar manner, gas fields may be polluted with H₂S
20 with the process having a similar construction as that of Example 1.

It goes without saying that the present invention is not limited to the examples mentioned, but rather that the invention extends to other exemplary embodiments that fall within
25 the protective scope of the claims.

CLAIMS

1. A method for the removal of a component from a process gas stream by contacting the same with a solvent for the component to be removed, followed by desorption of the dissolved component, **characterized** in that as solvent isotropic liquid crystals are used.

2. A method according to claim 1, **characterized** in that the component to be removed is dissolved in the liquid crystals that are in the isotropic state, after which the isotropic state undergoes a phase change to the nematic state under the influence of heat dissipation and/or pressure, with the result that the solubility of the gas to be removed in the liquid crystals is drastically reduced, such that the component to be removed for the most part desorbs, leaving the liquid crystals sufficiently free of component to be removed, after which they can be reused.

3. A method according to claims 1 and 2, **characterized** in that the phase change is realized by lowering the temperature or raising the pressure.

4. A method according to claims 1 and 2, **characterized** in that as solvent ionic liquid crystals are used that may be comprised of cations and anions (such as ionic liquids) or they may be zwitterions.

5. A method according to claim 1 or 2, **characterized** in that instead of applying the isotropic-nematic phase change, the isotropic-smectic phase change or the nematic-smectic phase change is applied (or a combination of these, such as isotropic-nematic-smectic).

6. A method according to one of the preceding claims 1-3, **characterized** in that the component to be removed is CO₂, H₂S, H₂O etc. or a mixture of these.

7. A method according to one of the preceding claims 1-5, **characterized** in that CO₂ is removed.

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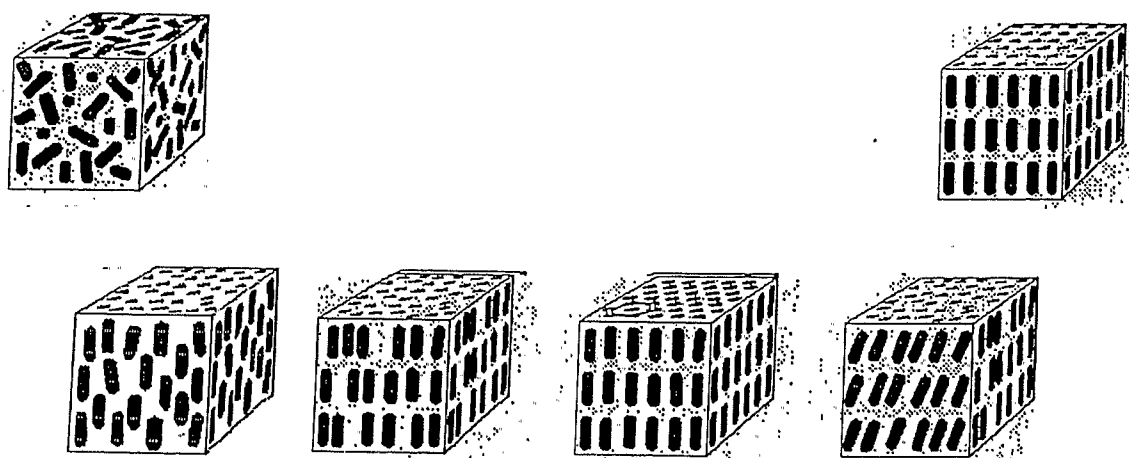


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2008/050145

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D53/14 B01D53/02 B01J20/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SUSANN M. BRANDER ET AL: "Reactive Foams for Air Purification" ENVIRON. SCI. TECHNOL., vol. 18, no. 4, 30 April 1984 (1984-04-30), - 30 April 1984 (1984-04-30) pages 224-230, XP002461420	1
A	page 224, paragraph 1 - page 224, paragraph 2 page 229, paragraph 4 - page 230, paragraph 3	2-7
A	----- US 2005/244665 A1 (RIVETT ET AL) 3 November 2005 (2005-11-03) page 2, paragraph 25 - page 3, paragraph 46; claims 1,9,11,18 ----- -/--	1

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/013119 A (SAES GETTERS S.P.A.) 1 February 2007 (2007-02-01) page 4, line 16 - page 8, line 5	1,6,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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WO 2007013119 A	01-02-2007	CN 101222977 A	16-07-2008
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