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**Datasheet for the decision
of 9 October 2015**

Case Number: T 1181/12 - 3.3.05

Application Number: 00117437.4

Publication Number: 1076035

IPC: C01B3/56, B01D53/047

Language of the proceedings: EN

Title of invention:

Pressure swing adsorption process for the production of hydrogen

Patent Proprietor:

PRAXAIR TECHNOLOGY, INC.

Opponent:

L AIR LIQUIDE SOCIETE ANONYME POUR L ETUDE ET L
EXPLOITATION DES PROCEDES GEORGES CLAUDE

Headword:

Relevant legal provisions:

EPC Art. 56, 115

Keyword:

Inventive step - (yes)
Observations by third parties not taken into consideration

Decisions cited:

T 0197/86, T 1756/11

Catchword:



**Beschwerdekammern
Boards of Appeal
Chambres de recours**

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Case Number: T 1181/12 - 3.3.05

**D E C I S I O N
of Technical Board of Appeal 3.3.05
of 9 October 2015**

Appellant: L AIR LIQUIDE SOCIETE ANONYME POUR L ETUDE ET L
(Opponent) EXPLOITATION DES PROCEDES GEORGES CLAUDE
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Decision under appeal: **Decision of the Opposition Division of the
European Patent Office posted on 28 March 2012
rejecting the opposition filed against European
patent No. 1076035 pursuant to Article 101(2)
EPC.**

Composition of the Board:

Chairman G. Rath
Members: G. Glod
P. Guntz

Summary of Facts and Submissions

I. The present appeal lies from the decision of the opposition division to reject the opposition against European patent No. EP-B-1 076 035.

The following documents were cited in the decision.

D1: EP-A-0 923 976

D2: EP-A-0 832 678

D3: EP-B-0 078 966

II. The opponent (hereinafter: appellant) filed an appeal against said decision and submitted grounds for the appeal.

III. With a letter of 29 November 2012 the patent proprietor (hereinafter: respondent) filed a reply and submitted six auxiliary requests.

IV. Third-party observations were filed anonymously on 8 October 2014.

V. With a letter of 18 December 2014, the respondent commented on the third-party observations.

VI. Further third-party observations were filed anonymously on 30 April 2014.

VII. In its communication under Article 15(1) of the Rules of Procedure of the Boards of Appeal (RPBA), the Board expressed its preliminary non-binding opinion that it was not convinced that the problem underlying the patent in suit as stated in paragraph 19 was solved. Therefore, the subject-matter of claim 1 appeared to be an obvious alternative in view of D3.

- VIII. By letter dated 14 August 2015, the respondent submitted further arguments and comparative hydrogen-PSA (pressure swing adsorption) simulations.
- IX. Oral proceedings took place on 9 October 2015. The respondent made auxiliary request 2, submitted with the letter of 29 November 2012, his sole request.

Independent claim 1 reads as follows:

"1. A pressure swing adsorption (PSA) process for purifying a feed gas stream containing more than 50 mole % hydrogen, which comprises passing the feed gas stream at a pressure above atmospheric pressure through a multilayer adsorbent bed, wherein at least one contaminant from the group H₂O, CO₂, CH₄ and CO is adsorbed from the feed gas stream prior to posing the stream through a layer of zeolite adsorbent,

characterized in that:

- (a) in the step of adsorbing at least one contaminant from the group H₂O, CO₂, CH₄ and CO from the feed gas stream the CO₂ content of the feed gas stream is reduced to less than 0.15 mole %, and*
- (b) in the step of passing the stream through a layer of zeolite adsorbent the feed gas stream is passed through a layer consisting of synthetic zeolite CaX adsorbent having a SiO₂ /Al₂O₃ ratio of 2.0-2.5 and exchanged at least 90% with calcium, wherein substantially all of the nitrogen in such stream is adsorbed and purified hydrogen having a purity of at least 99.9 % is recovered as product from the multilayer adsorbent bed."*

Claims 2 to 8 represent particular embodiments of the process of claim 1 on which they depend.

X. The arguments of the **appellant** can be summarised as follows:

D3 could be considered as closest prior art, since it related to the same technical field and had the same goal as the patent in suit.

It disclosed all the features of claim 1, except that it was not explicitly mentioned that the synthetic zeolite CaX was exchanged at least 90% with calcium and the purified hydrogen had a purity of at least 99.9%. In addition, the reduction of the CO₂ content of the feed gas to less than 0.15 mole% was not disclosed in D3.

D3 did not show a technical effect with respect to D3. Table 3 of the submissions of 14 August 2015 showed that D3 also allowed to obtain very pure hydrogen (99.998%) with substantially no nitrogen (9.5 ppmv). Furthermore, it was not credible that reducing the content of CO₂ to less than 0.15 mole% provided better results than 0.16 mole%.

Example B of D3 would lead the skilled person to an exchange of CaX of over 90%. In addition, it was known to the skilled person that nitrogen was poorly adsorbed in the presence of CO₂, as evidenced by D4 (US 2 882 244). Therefore, the skilled person would have reduced the content of CO₂ to less than 0.15 mole%. One way of achieving this was to increase the amount of active carbon. This could be arrived at by simple optimisation.

D1 showed in Table 1 that ratios of active carbon/zeolite of >1 were commonly used in the prior art.

D2 also suggested a CO₂ content of less than 0.1 ppm prior to the adsorbing step on zeolite.

The documents submitted by the third party would confirm the position of the appellant.

XI. The arguments of the **respondent** can be summarised as follows.

D3 did not disclose the level of the reduction in CO₂ content, the exchange level of the synthetic zeolite CaX adsorbent or that the zeolite adsorbent consisted of CaX adsorbent.

Zeolite X of sample B contained 20% by weight of zeolite A. In D3, only the overall Ca exchange level was specified. The actual Ca exchange level of the X zeolite in the zeolite mixture of D3 was unknown.

The findings of the Adsorption-Desorption test used in D3 to evaluate the samples showed that samples of class B with CaO/Al₂O₃ > 0.5 had improved performance compared with sample A. The ranking was Sample B > Sample C > Sample A. The teaching of D3 was towards a mixture of CaX with CaA.

The carbon/zeolite ratio used in document D3 was significantly lower than 1.

The value of less than 0.15 mole % was clearly not arbitrary, since it effectively defined the carbon/zeolite ratio used in the hydrogen-PSA (pressure swing adsorption) process. The patent aimed at improving the layering of the multilayer adsorbent bed and provided for substantial cost savings over the prior art approaches. The CO₂ limitation of less than 0.15 mole %

defined an adsorber design which in comparison with the designs employed in the prior art, such as in D3, contained more adsorbent for the preliminary contaminant removal step (such as activated carbon) and less zeolite. In the inventive examples the carbon/zeolite ratio was at least 1.95 by mass.

From the prior art one would have expected that increasing the ratio of carbon to zeolite adsorbents only would have been possible at the expense of adsorption performance. The design according to the invention provided greater hydrogen recovery and greater cycle times, so that it is beneficial from an economic and performance point of view.

The hydrogen-PSA simulations performed using the method described in paragraph 37 showed that document D3 did not permit to obtain the CO₂ limitation of < 0.15 mole % and that the hydrogen recovery was significantly reduced when compared with the present invention.

D1 did not disclose a larger active carbon bed in Figure 2 and did not disclose 99.9% hydrogen purity in Table 1.

D4 did not teach any specific level of CO₂ content.

The combination of D3 with D2 was not possible, since D2 was concerned with a process for argon purification using cryogenic temperatures. It was obvious to remove H₂O and CO₂ prior to cooling in such a process to avoid freezing of these components.

The prior art did not lead the skilled person to a CO₂ limitation of < 0.15 mole %.

The third-party observations should not be admitted, since they were filed anonymously. In addition, the documents were filed late and *prima facie* not relevant.

XII. Requests:

The **appellant (opponent)** requested that the decision under appeal be set aside and that the European patent be revoked.

The **respondent (patent proprietor)** requested that the patent be maintained in amended form on the basis of the set of claims of the sole request, submitted as auxiliary request 2 with the letter of 29 November 2012. All other requests were withdrawn.

Reasons for the Decision

1. Article 56 EPC

1.1 Invention

The invention concerns a pressure swing adsorption (PSA) process for producing high purity hydrogen from impure gas streams containing more than 50 mole% hydrogen.

1.2 Closest prior art

D3 (EP-B-0 078 966) is considered to be the closest prior art, since it also discloses an improved (column 4, lines 53 to 59) pressure swing adsorption process for producing hydrogen (column 2, lines 46 and 47), wherein a zeolite Ca-zeolite X granulate is used; at least about 50% of the Na initially present in the zeolite has been replaced by calcium (claim 1).

Specific adsorbents are selected for the various adsorbates so that drying is carried out with aluminum oxide or with silica gel and the removal of CO₂ and CH₄ with activated carbon (column 1, lines 31 to 39).

1.3 Problem

According to the patent in suit, the problem was to provide an **improved PSA process** for the production of hydrogen from an impure gas stream containing more than 50 mole % hydrogen (paragraph 19).

1.4 Solution

As a solution to this problem, a process according to claim 1 is proposed, characterised in that the CO₂ content of the feed gas stream is reduced to less than 0.15 mole %, the synthetic zeolite CaX is exchanged at least 90% with calcium and the recovered hydrogen has a purity of at least 99.9%.

1.5 Success of the solution

The examples of the patent in suit show that the use of the CaX(2.0) adsorbent leads to an improved H₂-recovery compared with the other adsorbents (LiX, VSA6, 5A) tested. In addition, CaX has the lowest bed size factor (Table 6).

The ratio of carbon/zeolite (3.25) used in example 1 of the patent is considerably different from the ratio in D3 (Table 2: 0.43 and 0.58). Since active carbon is less expensive than zeolite, the reversal of the ratio allows a reduction in costs.

The simulations submitted as a reaction to the

communication under Article 15(1) RPBA with the letter of 14 August 2015 (Table 3) show that a ratio of carbon/zeolite of 3 as compared with 0.5 leads to a CO₂ content at the end of the active carbon layer that meets the requirement of claim 1, i.e. less than 0.15 mole % (namely 0.001 mole %) compared with 0.57 mol % (in D3) and allows to obtain a higher H₂-recovery. In other words, running the configuration of D3 under conditions that allow to obtain 99.998% purity leads to an H₂-recovery (75.24%) that is well below the H₂-recovery (79.12%) obtained with a configuration according to the invention. The configuration according to D3 has a shorter cycle time (1520 s) than the configuration according to the invention (1640 s). These results are also confirmed (see Table 5 of the letter dated 14 August 2015) when running the configuration of D3 with a different active carbon that is similar to the material (Supersorbon) mentioned in D3.

As to the criticality of the value of 0.15 mol %, the appellant argued that the CO₂ reduction of feedstream to 0.15 mol% was arbitrary. However, it is not necessary to show that reducing the content of CO₂ to less than 0.15 mole % provides better results than a reduction to 0.16 mole %. It is established jurisprudence that if comparative tests are chosen to demonstrate an inventive step with an improved effect over a claimed area, the nature of the comparison with the closest state of the art must be such that the effect is convincingly shown to have its origin in the distinguishing feature of the invention (T 197/86, Reasons 6.1.3). This has been achieved by the simulations submitted with the letter of 14 August 2015 . These simulations show that in a set-

up according to D3 the CO₂-concentration at the end of the adsorption step is much higher than 0.15 mole % if the same product purity as in the present invention has to be obtained. The simulations representing the closest prior art were run with a zeolite falling within the scope of claim 1 of D3 and with two different types of active carbon, so that they can be considered as an acceptable representation of the closest prior art. There is no evidence that a reduction to 0.16 mole % CO₂ after the active carbon adsorption step could be achieved by a set-up according to the closest prior art D3. In addition, it has not been shown that the configuration according to D3 allows to obtain the same H₂-recovery than the process according to claim 1.

In view of these results and the lack of evidence to the contrary, the board accepts that a reduction of the carbon dioxide content to less than 0.15 mole % prior to passing the gas to the zeolite has economic and performance benefits. Therefore, it can be accepted that the problem has been successfully solved.

1.6 Obviousness

- 1.6.1 The question is whether in the prior art there were pointers (a) to the importance of reducing the CO₂ content of the feed gas stream to less than 0.15 mole % prior to passing it to the zeolite adsorbent and (b) to the high exchange rate of at least 90% with calcium in the synthetic zeolite CaX for the production of hydrogen having a purity of at least 99.9%. The gist of the invention was (1) to use more carbon and less zeolite than the prior art and (2) to still achieve higher H₂-recovery (paragraph 22).

1.6.2 D3 teaches that specific adsorbents are selected for the various adsorbates (column 1, lines 31 to 35). It is evident that the skilled person trying to solve the posed problem would optimise each adsorption step. However, D3 is completely silent about the optimisation of the drying step and the removal of CO₂ and CH₄ with activated carbon. It rather concentrates on the different types of zeolites (column 2, lines 5 to 19 and column 4, lines 14 to 22).

It may be accepted that the skilled person would optimise the process conditions in every adsorption step, but it is not plausible that the skilled person would completely change the mass ratio between the different adsorbents. As credibly explained by the respondent, the value of 0.15 mole % is only obtainable if the amount of carbon compared with zeolite is increased. The value of 0.15 mole % corresponds to an adsorber design which, in comparison with the design of D3, contains more adsorbent for the preliminary contaminant removal step and less zeolite. This is also in line with the results presented in the letter of 14 August 2015.

D3 teaches that the CaX zeolite adsorbent should be exchanged at least 50% with calcium in a process for the production of very pure H₂ (claim 1). The preferred range given in claim 4 is from 50% up to 100% exchange. The skilled person understands that any CaX zeolite adsorbent being exchanged from 50% to 100% with calcium is suitable for producing very pure H₂. The examples show that sample B, that is a combination of 20 % zeolite A with 80% CaX having a SiO₂/Al₂O₃ ratio of 2.5, provides the best performance (Tables 1 and 2). No details about the purity of H₂ obtained are given.

Based on the teaching of D3, the skilled person trying to solve the posed problem would use a zeolite according to sample B to obtain the best performance. A change in the amount of active carbon would not be considered, since there is no pointer thereto in D3. The combination of a synthetic zeolite CaX that is exchanged at least 90% with calcium with a process step that reduces CO₂ to less than 0.15 mole % prior to passing it to the zeolite is not taught in D3.

1.6.3 D1 also relates to a PSA-system for the production of hydrogen gas. The examples were conducted with three layers of adsorbents in a four-bed PSA process. The mass ratio of carbon/zeolite (900/514) was 1.75 (Tables 1 and 2). The hydrogen purity was 99.55% and 99.6%, respectively, which is below the 99.9% required by the solution of the present invention. D1 is completely silent about the role of the carbon/zeolite ratio and the amount of CO₂ after the active carbon adsorbent on the H₂-recovery. Rather, it teaches that a higher H₂-recovery in the four-bed PSA process can be obtained by using segregated tanks for concentration reversal (paragraph 36). Therefore, D1 does not provide the skilled person with a pointer to the present solution.

1.6.4 D2 relates to the removal of atmospheric gas impurities from an inert gas stream. It cannot be combined with D3, since it relates to a process different from that of D3, namely argon purification using cryogenic temperatures. In the process according to D2, CO₂ needs to be removed, since it would otherwise freeze in the cryogenic step. The problem underlying D2 is thus completely different from D3. It does not teach that the removal of CO₂ to less than 0.15 mole% in the purification of hydrogen as disclosed in D3 has

advantages on the H₂-recovery. D2 does not teach towards the proposed solution either.

1.6.5 D4 concerns zeolites, especially zeolite X. D4 does not relate to a process for producing hydrogen having a purity of at least 99.9%. D4 only teaches that carbon dioxide is more strongly adsorbed than hydrogen, helium, nitrogen, oxygen, methane, ethane and ethylene on zeolite X (column 14, lines 61 to 63). Thus, at most it suggests that, if nitrogen is to be removed by adsorption to zeolite from a gas containing CO₂ and nitrogen, then CO₂ should be removed prior to passing the gas through the zeolite bed. This is in line with the teaching of D3 (column 1, lines 35 to 42) and does not add anything more. It does not provide any indication that removing CO₂ to less than 0.15 mole% in a feed gas stream prior to passing it to the zeolite stream is beneficial in a process for producing very pure hydrogen. The skilled person starting from D3 does not get any new information in D4.

1.6.6 Therefore, the solution to the problem is not obvious and claim 1 involves an inventive step.

The same applies to dependent claims 2 to 8.

2. Third-party observations

Third-party observations were submitted anonymously during appeal proceedings after the reply of the respondent. In reply to the summons to oral proceedings, the appellant argued that the third-party observations confirmed what they had already submitted in their statement of grounds of appeal. The appellant did not specifically rely on any of the documents cited by the third party to present its case and did not

provide any arguments why these documents were relevant for the decision and should be admitted into the proceedings.

Therefore, in agreement with T 1756/11 (reasons 2.9 to 2.11), the third-party observations have not been taken into consideration.

Order

For these reasons it is decided that:

1. The decision under appeal is set aside.
2. The case is remitted to the opposition division with the order to maintain the patent on the basis of claims 1 to 8 of the sole request, submitted as auxiliary request 2 with the letter of 29 November 2012, and a description and figures to be adapted where necessary.

The Registrar:

The Chairman:



C. Vodz

G. Rath

Decision electronically authenticated