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(54) **Title**: METHOD OF MAKING PURIFIED METHANOL FROM A LIQUEFIED FRACTION OBTAINED FROM A SULFATE PULP PROCESS

(57) **Abstract**: The invention relates to a method for making purified methanol from a liquefied fraction obtained from a sulfate pulp process and containing methanol and sulfur contaminants, its main sulfur contaminants being methyl mercaptan, dimethyl sulfide and dimethyl disulfide. According to the invention, the fraction is subjected to an oxidation treatment, followed by separating the methanol by distillation or water vapor distillation from distillation residue containing sulfur-bearing oxidation products. From the distillation residue can be crystallized dimethyl sulfone produced in oxidation and obtained as a by-product of the process.

Method of making purified methanol from a liquefied fraction obtained from a sulfate pulp process

The present invention relates to a method of making purified methanol from a liquefied fraction obtained from a sulfate pulp process and containing methanol and sulfur contaminants, its main organic sulfur contaminants being methyl mercaptan, dimethyl sulfide and dimethyl disulfide.

Traditionally, methanol has been made by the dry distillation of wood, producing charcoal along with methanol. However, this methanol making process has become redundant because of its costliness and poor yield.

At present, methanol is manufactured industrially from a synthesis gas consisting of carbon monoxide and hydrogen. Wood is one of the suggested sources of synthesis gas, wherein wood is gasified with oxygen and the obtained gas is reformed catalytically and cleaned of contaminants to produce a mixture of carbon monoxide and hydrogen suitable for methanol synthesis.

In forest industry, methanol present in wood is also released at different stages of the sulfate pulp process. Already at the cooking stage there are generated condensable vapors, which contain methanol, but the bulk of methanol remains in the black liquor and are released during evaporation of the same, ending up in a so called foul condensate at the evaporation plant. Other condensates from the process are combined with the foul condensate, and these are fractionated by steam distillation into water and a gaseous fraction, which is liquefied. The main composition of the liquefied fraction is > 50 weight-% (typically about 55 weight-%) of methanol, < 10 weight-% of ethanol, < 5 weight-% of acetone, about 10 weight-% of sulfur contaminants, and the balance (typically about 20 weight-%) is water. A typical composition of sulfur contaminants is in turn < 50 weight-% of methyl mercaptan, < 30 weight-% of dimethyl sulfide, < 20 weight-% of hydrogen sulfide, and < 10 weight-% of dimethyl disulfide.

A problem regarding viable utilization of methanol derived from the sulfate process is effective removal of sulfur compounds, both distillation and steam distillation being inadequate therefor. The boiling points of methyl mercaptan and dimethyl sulfide are lower than those of methanol and those compounds should be separated by distillation prior to the distillation of methanol. Otherwise they would become distilled along with methanol. On the other hand, the boiling point of

dimethyl disulfide is higher than that of methanol, being therefore left in the distillation residue in methanol distillation. For obtaining pure methanol several distillation cycles would be required, making the refining process inconvenient and inefficient.

FI patent publication 52710 discloses a method for the purification of methanol separated from sulfate process condensates, comprising treating the condensate or impure methanol with sulfuric acid, distilling the methanol to separate it from water phase, oxidizing along-distilled sulfur impurities with hydrogen peroxide, and finally separating pure methanol by further distillation. Hence, the question is about a multiphase process, which the applicant does not find economically viable.

The removal of sulfur or sulfur compounds from alcohols, such as methanol or ethanol, has been described in publication US 2007/0238907 A1, wherein the sulfur compounds are adsorbed to the surface of a metal or metal alloy. Reference is made to Iron, copper and zinc as suitable metals. However, the sulfur compounds mentioned in the publication are solely inorganic. At least as such, the procedure cannot be expected to work for organic sulfur compounds.

For the above reasons, the liquefied fraction containing methanol has mostly been exploited by burning it in energy production. Being a sulfur-containing fuel, it has nevertheless been problematic in terms of environmental protection.

It is an object of the invention to provide a solution, whereby separation of methanol from the low-boiling organic sulfur contaminants of the liquefied methanol-containing fraction from the sulfate pulp process and thereby also the production of pure methanol become efficient and economically feasible. Thus, an object of the invention is to enable utilization of the steam distillation product of the foul condensate from a sulfate pulp process as a raw material in methanol production, such product having been regarded thus far as of low value or even problematic. The invention is characterized in that the liquefied methanol-containing fraction is subjected to an oxidation treatment, followed by separating the methanol by distillation or water vapor distillation from distillation residue containing sulfur-containing oxidation products.

The invention is based on the surprising finding that it is possible to oxidize sulfur compounds of low boiling point, such as methyl mercaptan (CH_3-S-H) and dimethyl sulfide (CH_3-S-CH_3), into higher boiling sulfur compounds without having

the present methanol oxidized at the same time. The removal of methanol can be subsequently conducted by distillation or water vapor distillation from sulfur-containing oxidation products, which are left in distillation residue. The oxidation products include dimethyl sulfoxide (CH_3-SO-CH_3) and dimethyl sulfone (CH_3-SO_2-CH_3), which are isolable from distillation residue and of which particularly dimethyl sulfone has value as a commercial product. The latter aspect is also a contributing factor to viability of the process as a way of making pure methanol.

Another major benefit of the invention is avoiding the disposal of the methanol fraction by burning and the environmental problems resulting therefrom.

The oxidation reactions of dimethyl sulfide into dimethyl sulfoxide or dimethyl sulfone are prior known as such. The oxidation of dimethyl sulfide with nitrogen tetroxide in water-free conditions is a known process of making dimethyl sulfoxide. The oxidation of sulfur compounds, such as hydrogen sulfide, methyl mercaptan and dimethyl sulfide, with hydrogen peroxide in waste water purification has been described in the article *Feliers, C., Patria, L., Morvan, J., Laplanche, A., Environmental Technology, Vol. 22, 2001, pp. 1137–1146.* The purpose is to reduce odor nuisances caused by sulfur compounds. The oxidation of dimethyl sulfide into dimethyl sulfoxide and dimethyl sulfone as an atmospheric photochemical reaction has been described, among others, in the article *Yin, F., Grosjean, D., Flagan, R.C., Seinfeld, J.H., Journal of Atmospheric Chemistry II, 1990, pp. 365–399.* None of these publications nevertheless discloses the oxidation of organic sulfur compounds, with methanol serving as a main liquid medium for the reaction.

Oxidants suitable for the purification process of the invention are peroxides, oxygen, ozone, chlorine, permanganate or hypochlorite, especially hydrogen peroxide.

The oxidation of sulfur compounds takes place in the invention most preferably in the presence of a metal-containing catalyst. The metal contained in the catalyst can be e.g. Fe, Cu or Zn, and it can be in its elemental state or in the form of a compound, such as oxide or sulfate. After the oxidation process, prior to distillation or water vapor distillation of methanol, the catalyst can be separated from liquid phase by filtration.

A preferred way of applying the invention is such that the liquefied methanol-containing fraction is first subjected to oxidation with hydrogen peroxide or the like suitable oxidant, preferably in the presence of a metal or metal compound catalyst. The catalyst is removed from the liquid reaction mixture by filtration, after which pure methanol is separated by distillation or water vapor distillation while sulfur-containing oxidation products are left in distillation residue. The aqueous distillation residue is exploitable preferably by crystallizing dimethyl sulfone therefrom as a valuable by-product of the process.

In oxidation, dimethyl sulfide oxidizes first into dimethyl sulfoxide, this being a fast exothermic reaction. Conversely, the oxidation of dimethyl sulfoxide in the next stage into dimethyl sulfone is a slow reaction, which nevertheless speeds up substantially by heating the reaction medium. Should the separation of methanol from reaction medium be commenced before the oxidation is completed, conveniently while the second process stage is still in progress, the distillation brings heat into the reaction medium, thus preferably accelerating at the same time the formation of dimethyl sulfone and thereby the completion of the process. Hence, whenever necessary, the supply of oxidant into the reaction mixture can also be continued even during the course of distillation.

The following working examples describe the oxidation of the methanol-containing fraction, which is a critical stage of the process. A successful oxidation converts the low-boiling sulfur contaminants, methyl mercaptan and dimethyl sulfide, into dimethyl sulfoxide and further into dimethyl sulfone, whereby pure methanol is capable of being distilled or water vapor distilled to remove it from distillation residue which retains the oxidized sulfur compounds.

Example 1

For the trials, in order to ensure comparability of the results, there was prepared a synthetic liquid mixture imitating the methanol-containing fraction obtainable from a sulfate pulp process, with a constant composition of methanol (67.3 volume-%), water (19.2 volume-%), ethanol (6.7 volume-%), and acetone (2.9 volume-%), as well as sulfur compounds dimethyl sulfide (2.9 volume-%) and dimethyl disulfide (1.0 volume-%). 25 ml of this condensate (pH 7.5) was measured into an Erlenmeyer (100 ml), to which was then added 0.72 g of metallic iron as a catalyst and 6 ml of 30 volume-% hydrogen peroxide as an oxidant. The resulting mixture was stirred at room temperature for one hour, allowed to stabilize for 10 minutes

without stirring, and filtered (filter's pore size 0.45 µm) for removing the catalyst. In order to demonstrate the oxidation product's crystallization effect, the mixture's methanol was allowed to evaporate gradually at room temperature at normal pressure, thus producing white crystals, which by a detailed X-ray diffraction analysis (D.E. Sands; Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem., 119(1963)245, D.A. Langs, J.V. Silverton and W.M. Bright; J. Chem. Soc. D., (1970)1653) were found to consist solely of pure dimethyl sulfone. On the other hand, the overall sulfur budget based on X-ray fluorescence measurement showed that the total yield of crystallized dimethyl sulfone was about 85 weight-% as calculated from initial sulfur. The negligible presence of inorganic sulfur compounds was confirmed ion chromatographically.

Example 2

Oxidation of a liquid mixture was conducted as in example 1, the only difference being that metal catalyst was not added to the mixture. Even in this case, the overall yield of dimethyl sulfone was found to remain at the level of 85 weight-%.

Example 3

Oxidations of a liquid mixture were conducted as in examples 1 and 2 with the difference that, prior to the oxidation, the pH of the mixture was adjusted with an aqueous solution of 25% sodium hydroxide to the value of 12. Even now, the total yield of dimethyl sulfone was about 85 weight-% in trials conducted both with catalysts and without a catalyst.

In order to simplify the conduction of laboratory trials, methanol has been allowed in the above examples 1–3 to separate by evaporation, but it is obvious for a skilled artisan that methanol is equally removable by distillation or water vapor distillation. The oxidized sulfur compounds, as well as water present in the reaction mixture, all have boiling points higher than that of methanol and remain in distillation residue.

Claims

1. A method for making purified methanol from a liquefied fraction obtained from a sulfate pulp process and containing methanol and sulfur contaminants, its main organic sulfur contaminants being methyl mercaptan, dimethyl sulfide and dimethyl disulfide, **characterized** in that the fraction is subjected to an oxidation treatment, followed by separating the methanol by distillation or water vapor distillation from distillation residue containing sulfur-containing oxidation products.

2. A method as set forth in claim 1, **characterized** in that the oxidant is peroxide, oxygen, ozone, chlorine, permanganate or hypochlorite, preferably hydrogen peroxide.

3. A method as set forth in claim 1 or 2, **characterized** in that the oxidation takes place in the presence of a metal-containing catalyst.

4. A method as set forth in claim 3, **characterized** in that prior to the distillation or water vapor distillation of methanol the catalyst is removed therefrom by filtration.

5. A method as set forth in claim 3 or 4, **characterized** in that the metal contained in the catalyst is Fe, Cu or Zn.

6. A method as set forth in any of claims 3-5, **characterized** in that the catalyst has its metal in elemental state or in the form of a compound, such as oxide or sulfate.

7. A method as set forth in any of the preceding claims, **characterized** in that, during the methanol removal conducted by distillation or water vapor distillation, the reaction medium is supplied with an oxidant, such as hydrogen peroxide, oxygen or air, for carrying the oxidation to completion.

8. A method as set forth in any of the preceding claims, **characterized** in that, the liquefied fraction forming the starting material contains > 50 weight-% of methanol, 2–10 weight-% of ethanol, 1–5 weight-% of acetone, and 5–15 weight-% of sulfur contaminants, the balance substantially consisting of water.

9. A method as set forth in claim 8, **characterized** in that the sulfur contaminants substantially consist of methyl mercaptan, dimethyl sulfide, hydrogen sulfide and dimethyl disulfide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2012/050100

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

IPC: C07C, D21C

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

SE, DK, FI, NO classes as above

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

EPO-Internal, PAJ, WPI data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SE 430411 B (KEMI OY), 14 November 1983 (1983-11-14); claim 1 --	1-9
X	US 20100316553 A1 (BRUCHER JORG ET AL), 16 December 2010 (2010-12-16); paragraph [0036]; claims 1, 7, 10 --	1-9
A	Dufresne R. et al., Treatment of Clean Condensate Using Catalytically Enhanced Oxidation, Proceedings of the 2000 TAPPI International Environmental Conference, page 89-101; Whole document --	1-9

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2012/050100

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WO 9735063 A1 (DOW CHEMICAL CO), 25 September 1997 (1997-09-25); claims 1-4	1-9
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International application No.
PCT/FI2012/050100

Continuation of: second sheet

International Patent Classification (IPC)

D21C 11/14 (2006.01)
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Cited literature, if any, will be enclosed in paper form.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2012/050100

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