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(54) Title: METHODS FOR REMOVING CONTAMINANTS FROM ALGAL OIL

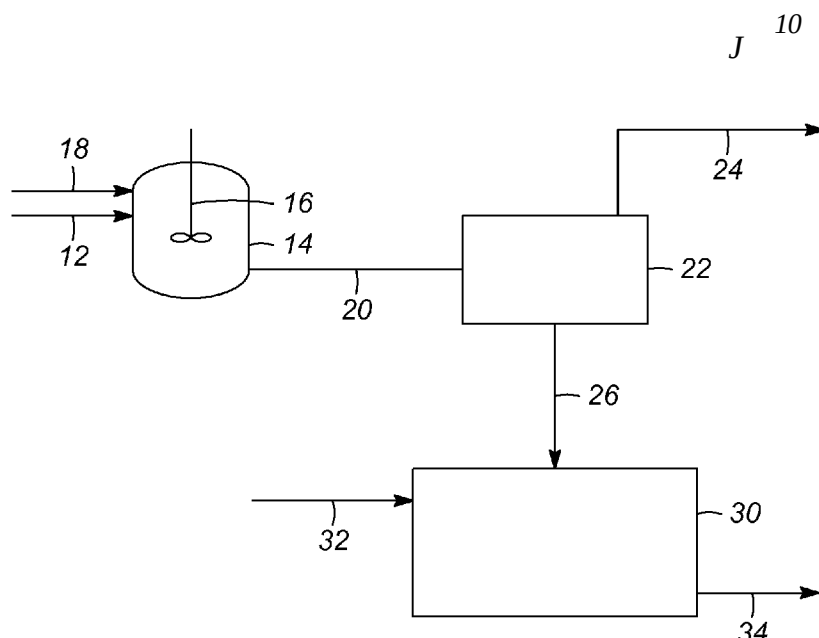


FIG. 1

(57) Abstract: Methods for removing contaminants from algal oil are provided. In an embodiment, a method comprises the steps of combining a sulfuric acid-aqueous solution that has a pH of 1 or less with a contaminant-containing algal oil at treatment conditions effective to form an effluent. The effluent comprises a treated algal oil phase and contaminants in an acidic aqueous phase. The contaminants comprise metals, phosphorus, or combinations thereof. The acidic aqueous phase is removed from the effluent to form a contaminant-depleted algal oil.



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ML, MR, NE, SN, TD, TG).

— *with international search report (Art. 21(3))*

## METHODS FOR REMOVING CONTAMINANTS FROM ALGAL OIL

## STATEMENT OF PRIORITY

5     **[0001]**   This application claims priority to U.S. Application No. 13/326,057 which was filed on December 14, 2011, the contents of which are hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
DEVELOPMENT

10    **[0002]**   This invention was made with Government support under DE-EE0003046 awarded by the U.S. Department of Energy. The Government has certain rights in this invention.

## TECHNICAL FIELD

15    **[0003]**   The present invention relates generally to methods for treating biomass-derived oils, and more particularly relates to methods for removing contaminants from algal oil to form a contaminant-depleted algal oil that can be further processed, for example, to produce a biofuel.

## BACKGROUND

20    **[0004]**   Algae are a diverse group of photosynthetic organisms that form a type of biomass that has attracted significant attention in recent years because of its ability to produce oil (hereinafter "algal oil"). Algal oil is rich in lipids and can be processed, e.g., via hydroprocessing and/or isomerization, to produce biofuels, such as bio-diesel, bio-jet, and the like.

25    **[0005]**   Many of the extraction methods employed to extract oil from non-algae biomass feedstocks, such as vegetables, seeds, and the like, are non-disruptive type methods. These non-disruptive type methods generally do not disrupt the biomass cells and tend to produce relatively clean oils, e.g., vegetable oils, canola oil, sunflower oil, etc., with a substantial portion of the contaminants remaining behind in the biomass cells after the oil has been removed. Unfortunately, these non-disruptive type methods do not work well

with algae because algae cells are relatively small, e.g., 2 to 20 nm, and have thick cell walls that make the extraction of algal oil more difficult.

**[0006]** Rather, algal oils are typically extracted from algae using disruptive type methods. Disruptive type methods include mechanical, thermal, enzymatic, or chemical methods that disrupt the algae cells to extract the algal oil as either a predominately lipid or esterified lipid oil or as liquefied algal biomass. However, by disrupting the algae cells, contaminants are readily removed from the algae cells together with the algal oil during extraction. These contaminants may include metals and phosphorus that are very problematic for downstream processing, such as processes for converting the algal oil to a biofuel. In particular, the metals and phosphorus contained in the algal oil are poisonous to many catalysts (e.g. hydroprocessing catalyst, isomerization catalyst, etc.) that are used to convert algal oils to biofuels. Unfortunately, current methods for removing contaminants from the algal oil prior to downstream oil conversion have proven to be unsatisfactory and currently limit the utilization of algal oils to produce biofuels.

**[0007]** Accordingly, it is desirable to provide methods for removing contaminants from algal oil to form a contaminant-depleted algal oil that may be further processed, for example, to produce a biofuel. Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background.

## BRIEF SUMMARY

**[0008]** Methods for removing contaminants from algal oil are provided herein. In accordance with an exemplary embodiment, a method for removing contaminants from algal oil comprises the steps of combining a sulfuric acid-aqueous solution that has a pH of 1 or less with a contaminant-containing algal oil at treatment conditions effective to form an effluent. The effluent comprises a treated algal oil phase and contaminants in an acidic aqueous phase. The contaminants comprise metals, phosphorus, or combinations thereof. The acidic aqueous phase is removed from the effluent to form a contaminant-depleted algal oil.

**[0009]** In accordance with another exemplary embodiment, a method for removing contaminants from algal oil is provided. The method comprises the steps of introducing a contaminant-containing algal oil and a sulfuric acid-aqueous solution that has a pH of 1 or

less to a reactor. The reactor is operating at treatment conditions effective to form an effluent. The effluent comprises a treated algal oil phase and contaminants in an acidic aqueous phase. The contaminants comprise metals, phosphorus, or combinations thereof. The effluent is introduced to an oil-water separation zone to remove the acidic aqueous phase from the effluent and form a contaminant-depleted algal oil.

**[0010]** In accordance with another exemplary embodiment, a method for removing contaminants from algal oil is provided. The method comprises the steps of introducing a contaminant-containing algal oil and a sulfuric acid-aqueous solution at a predetermined acid to oil ratio of from 1:4 to 4:1 to a reactor. The reactor is operating at treatment conditions effective to form an effluent. The effluent comprises a treated algal oil phase and contaminants in an acidic aqueous phase. The contaminants comprise metals, phosphorus, or combinations thereof. The sulfuric acid-aqueous solution comprises sulfuric acid that is present in an amount of from 1 to 50 wt. % of the sulfuric acid-aqueous solution. The predetermined acid to oil ratio is defined by a first weight of the sulfuric acid-aqueous solution to a second weight of the contaminant-containing algal oil. The effluent is introduced to an oil-water separation zone to remove the acidic aqueous phase from the effluent and form a contaminant-depleted algal oil.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0011]** The present invention will hereinafter be described in conjunction with the following drawing figures, wherein like numerals denote like elements, and wherein:

**[0012]** FIG. 1 is a block diagram of an apparatus for removing contaminants from algal oil in accordance with an exemplary embodiment.

#### DETAILED DESCRIPTION

**[0013]** The following Detailed Description is merely exemplary in nature and is not intended to limit the invention or the application and uses of the invention. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

**[0014]** Various embodiments contemplated herein relate to methods for removing contaminants from algal oil. Unlike the prior art, the exemplary embodiments taught herein combine a sulfuric acid-aqueous solution with a contaminant-containing algal oil at treatment conditions effective to form an effluent. The contaminants comprise metals

and/or phosphorus, such as Ca, Fe, Mg, Na, Zn, K, and/or P. The sulfuric acid-aqueous solution is a concentrated acidic solution having a pH of 1 or less. The inventor has found that the relatively low pH sulfuric acid-aqueous solution effectively digests the contaminants in the algal oil at the treatment conditions to form the effluent that comprises a treated algal oil phase and the contaminants digested in an acidic aqueous phase. The aqueous phase including the contaminants is removed from the effluent to form a contaminant-depleted algal oil. In an exemplary embodiment, the contaminant-depleted algal oil contains 10 weight percent (wt. %) or less of the contaminants that were originally present in the contaminant-containing algal oil. As such, the contaminant-depleted algal oil may be passed along for further processing, for example, to produce a biofuel.

**[0015]** Referring to FIG. 1, a schematic depiction of an apparatus 10 for removing contaminants from algal oil in accordance with an exemplary embodiment is provided. As illustrated, a contaminant-containing algal oil stream 12 is introduced to a reactor 14. The contaminant-containing algal oil stream 12 comprises algal oil and contaminants. In an exemplary embodiment, the contaminant-containing algal oil stream 12 is a stream containing crude algal oil (e.g. "as extracted" algal oil). The crude algal oil may be obtained via a mechanical, thermal, enzymatic, or chemical disruptive method that disrupts the algae cells to extract the algal oil as is well known or by any other method known to those skilled in the art. Crude algal oil is also commercially available, for example, from Solix BioSystems, Inc., which is headquartered in Fort Collins, Colorado.

**[0016]** In an exemplary embodiment, the contaminants in the contaminant-containing algal oil stream 12 comprise phosphorus and/or metals, such as Ca, Fe, Mg, Na, Zn, and/or K. The contaminants may also comprise other metals, such as Al, Co, Cr, Cu, Mn, Mo, Pb, Sn, Sr, Ti, and/or V. In an exemplary embodiment, the contaminant-containing algal oil stream 12 contains up to 8,000 ppm or greater of total contaminants.

**[0017]** The reactor 14 may be a batch reactor or a continuous flow reactor. In an exemplary embodiment, the reactor 14 is a continuous stirred tank reactor (CSTR) that includes a mechanical mixing device 16. Alternatively, the reactor 14 may be any other type of reactor known to those skilled in the art for removing contaminants from oil to produce treated oil.

**[0018]** A sulfuric acid-aqueous solution stream 18 is introduced to the reactor 14. The sulfuric acid-aqueous solution stream 18 comprises sulfuric acid and water. In an exemplary embodiment, the sulfuric acid-aqueous solution stream 18 comprises sulfuric acid that is present in an amount of from 1 to 50 wt. %, for example from 2 to 50 wt. %, for example from 5 to 15 wt. %, such as 10 wt. % of the sulfuric acid-aqueous solution stream 18. In an exemplary embodiment, the sulfuric acid-aqueous solution stream 18 has a pH of 1 or less, for example from 1 to -1, for example from 0 to -0.5, such as -0.1.

**[0019]** The sulfuric acid-aqueous solution stream 18 and the contaminant-containing algal oil stream 12 are introduced to the reactor at a predetermined acid to oil ratio. The predetermined acid to oil ratio is defined by a mass flow rate of the sulfuric acid-aqueous solution stream 18 to a mass flow rate of the contaminant-containing algal oil stream 12 (e.g. effectively a weight of the sulfuric acid-aqueous solution added to the reactor 14 to a weight of the contaminant-containing algal oil added to the reactor 14). In an exemplary embodiment, the predetermined acid to oil ratio is from 1:4 to 4:1, for example from 1:2 to 2:1, such as 1:1.

**[0020]** As illustrated, the sulfuric acid-aqueous solution stream 18 and the contaminant-containing algal oil stream 12 are combined in the reactor 14 and agitated with the mechanical mixing device 16. The reactor 14 is operating at treatment conditions effective for the sulfuric acid-aqueous solution to digest the contaminants in the contaminant-containing algal oil to form an effluent 20. The effluent 20 comprises a treated algal oil phase and an acidic aqueous phase. The treated algal oil phase is substantially depleted of the contaminants that are now digested and substantially present in the acidic aqueous phase. In an exemplary embodiment, the treatment conditions include a temperature of from 15 to 45°C, a pressure of from 80 to 120 kPa, and a residence time of from 30 minutes to 8 hours, for example from 1 to 5 hours, such as from 1 to 2 hours. The residence time is defined by an amount of time that the contaminant-containing algal oil and the sulfuric acid-aqueous solution are in contact with each other in the reactor 14 to form the effluent 20.

**[0021]** The effluent 20 is introduced to an oil-water separation zone 22. The oil-water separation zone 22 removes the acidic aqueous phase including the contaminants from the effluent 20 using one or more separation vessels, fractionation columns, heaters, condensers exchangers, pipes, pumps, compressors, controllers, and/or the like. In an

exemplary embodiment, the oil-water separation zone 22 comprises an American Petroleum Institute (API) oil-water separator that separates the effluent 20 based on the specific gravity difference between the treated algal oil phase and the acidic aqueous phase. As illustrated, the oil-water separation zone 22 separates the effluent 20 to form a  
5 contaminant-depleted algal oil stream 24 and an acidic contaminant-containing aqueous solution stream 26.

**[0022]** In an exemplary embodiment, the contaminant-depleted algal oil stream 24 contains 10 wt. % or less, for example 6 wt. % or less, for example 4 wt. % or less, for example 2 wt. % or less, such as from 1 to 0 wt. % of the contaminants that were  
10 originally present in the contaminant-containing algal oil stream 12. That is, for example, the contaminant-depleted algal oil stream 24 is algal oil that has been treated such that 90 wt. % or greater, for example 94 wt. % or greater, for example 96 wt. % or greater, for example 98 wt. % or greater, such as 99 to 100 wt. % of the contaminants originally present in the crude algal oil have been removed. The contaminant-depleted algal oil  
15 stream 24 is removed from the oil-water separation zone 22 and is passed along, for example, for further processing to produce a biofuel.

**[0023]** The acidic contaminant-containing aqueous solution stream 26 is removed from the oil-water separation zone 22 and is passed along and introduced to neutralizing zone 30. A base-containing composition 32 is introduced to the neutralizing zone 30. In an  
20 exemplary embodiment, the base-containing composition 32 is a solution having a pH of 10 or greater, such as 10 to 14. In one example, the base-containing composition 32 is a sodium hydroxide aqueous solution that has a pH of 10 to 12. The base-containing composition contacts and neutralizes the acidic contaminant-containing aqueous solution stream 26 to form a salty contaminant-containing aqueous solution stream 34. The salty  
25 contaminant-containing aqueous solution stream 34 is removed from the neutralizing zone 30 for disposal.

**[0024]** Accordingly, methods for removing contaminants from algal oil have been described. Unlike the prior art, the exemplary embodiments taught herein combined a sulfuric acid-aqueous solution with a contaminant-containing algal oil at treatment  
30 conditions effective to form an effluent. The contaminants comprise metals and/or phosphorus, and the sulfuric acid-aqueous solution is a concentrated acidic solution having a pH of 1 or less. The relatively low pH sulfuric acid-aqueous solution effectively digests

the contaminants in the algal oil at the treatment conditions to form the effluent that comprises a treated algal oil phase and the contaminants digested in an acidic aqueous phase. The aqueous phase including the contaminants is removed from the effluent to form a contaminant-depleted algal oil. In an exemplary embodiment, the contaminant-

5 depleted algal oil contains 10 weight percent (wt. %) or less of the contaminants that were originally present in the contaminant-containing algal oil. As such, the contaminant-depleted algal oil may be passed along for further processing, for example, to produce a biofuel.

[0025] While at least one exemplary embodiment has been presented in the foregoing

10 detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for

15 implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

## CLAIMS

What is claimed is:

1. A method for removing contaminants from algal oil, the method  
5 comprising the steps of:  
combining a sulfuric acid-aqueous solution (18) that has a pH of 1 or less  
with a contaminant-containing algal oil (12) at treatment conditions effective to  
form an effluent (20) that comprises a treated algal oil phase and contaminants in  
an acidic aqueous phase, wherein the contaminants comprise metals, phosphorus,  
10 or combinations thereof; and  
removing the acidic aqueous phase from the effluent (20) to form a  
contaminant-depleted algal oil (24).
2. The method of claim 1, wherein the step of combining comprises  
15 combining the sulfuric acid-aqueous solution (18) that has the pH of from 1 to -1  
with the contaminant-containing algal oil (12).
3. The method of claim 1, wherein the step of combining comprises  
20 combining the sulfuric acid-aqueous solution (18) with the contaminant-containing  
algal oil (12) at the treatment conditions that include a residence time of from 30  
minutes to 8 hours, wherein the residence time is defined by an amount of time that  
the contaminant-containing algal oil (12) is in contact with the sulfuric acid-  
aqueous solution (18) to form the effluent (20).
- 25 4. The method of claim 1, wherein the step of combining comprises  
combining the sulfuric acid-aqueous solution (18) with the contaminant-containing  
algal oil (12) at the treatment conditions that include a temperature of from 15 to  
45°C.
- 30 5. The method of claim 1, wherein the step of combining comprises  
combining the sulfuric acid-aqueous solution (18) with the contaminant-containing  
algal oil (12) at a predetermined acid to oil ratio of from 1:4 to 4:1, wherein the

predetermined acid to oil ratio is defined by a first weight of the sulfuric acid-aqueous solution (18) to a second weight of the contaminant-containing algal oil (12).

5           6.       The method of claim 5, wherein the step of combining comprises combining the sulfuric acid-aqueous solution (18) with the contaminant-containing algal oil (12) at the predetermined acid to oil ratio of from 1:2 to 2:1.

10          7.       The method of claim 1, wherein the step of combining comprises combining the contaminant-containing algal oil (12) with the sulfuric acid-aqueous solution (18) that comprises sulfuric acid present in an amount of from 1 to 50 wt. % of the sulfuric acid-aqueous solution (18).

15          8.       The method of claim 1, wherein the step of removing comprises separating the acidic aqueous phase from the effluent (20) to form an acidic contaminant-containing aqueous solution (26), and the method further comprises the step of:  
              introducing a base-containing composition (32) to the acidic contaminant-containing aqueous solution (26) to neutralize the acidic contaminant-containing aqueous solution (26).

20          9.       The method of claim 1, wherein the step of combining comprises combining the sulfuric acid-aqueous solution (18) with the contaminant-containing algal oil (12) that contains the contaminants comprising Ca, Fe, Mg, Na, Zn, K, P, or combinations thereof.

25          10.      The method of claim 1, wherein the step of removing comprises forming the contaminant-depleted algal oil (24) containing 10 wt. % or less of the contaminants that were originally present in the contaminant-containing algal oil (12).

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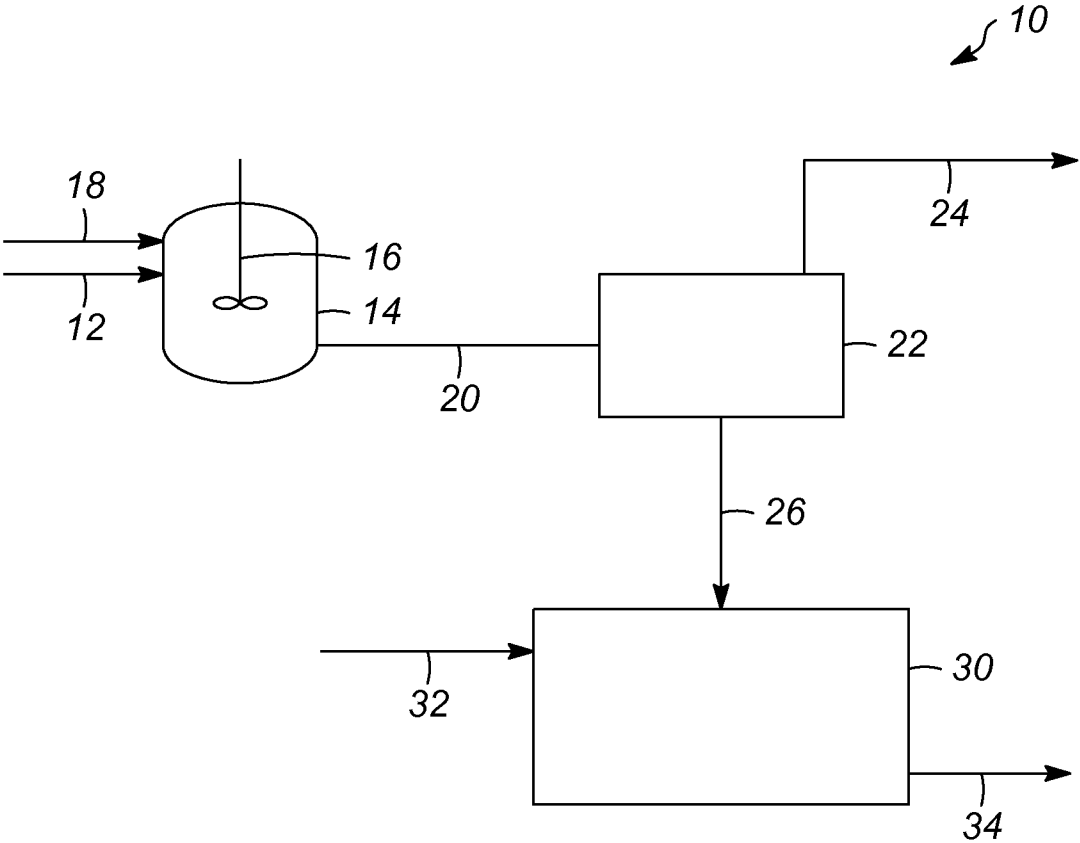


FIG. 1

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2012/053751

## A. CLASSIFICATION OF SUBJECT MATTER

**CUB 3/00** (2006.01)**CUB 3/04** (2006.01)**CUB 3/06** (2006.01)**CIOL 1/00** (2006.01)

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)

C I I B 3/00, 3/04, 3/06, C I O L 1/00

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 practicable, search terms used)

PatSearch (RU PTO internal), Esp@cenet, PAJ, USPTO

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                     | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 2011/0047866 A1 (CONOCOPHILLIPS COMPANY) 03.03.2011, par. 0013, 0015, 0025-0027, claim 19, examples | 1-4, 7, 9, 10         |
| Y         |                                                                                                        | 5, 6, 8               |
| Y         | US 2011/0086386 A1 (THOMAS J. CZARTOSKI et al.) 14.04.2011, claims 5, 6, examples                      | 5, 6, 8               |
| A         | US 2008/0197052 A1 (CLAYTON V. MCNEFF et al.) 21.08.2008                                               | 1-10                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents:

|     |                                                                                                                                                                     |     |                                                                                                                                                                                                                                              |
|-----|---------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| "A" | document defining the general state of the art which is not considered to be of particular relevance                                                                | "T" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention                                              |
| "E" | earlier document but published on or after the international filing date                                                                                            | "X" | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone                                                                     |
| "L" | document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| "O" | document referring to an oral disclosure, use, exhibition or other means                                                                                            | "&" | document member of the same patent family                                                                                                                                                                                                    |
| "P" | document published prior to the international filing date but later than the priority date claimed                                                                  |     |                                                                                                                                                                                                                                              |

Date of the actual completion of the international search

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