(19) DANMARK

(10) **DK/EP 3526316 T3**

Patent- og
Varemærkestyrelsen

(12) Oversættelse af
europæisk patentskrift

(51) Int.Cl.: ***C 10 L 3/08 (2006.01)*** ***A 01 K 61/00 (2017.01)***

(45) Oversættelsen bekendtgjort den: **2020-12-21**

(80) Dato for Den Europæiske Patentmyndigheds
bekendtgørelse om meddelelse af patentet: **2020-09-30**

(86) Europæisk ansøgning nr.: **17807942.2**

(86) Europæisk indleveringsdag: **2017-10-13**

(87) Den europæiske ansøgnings publiceringsdag: **2019-08-21**

(86) International ansøgning nr.: **NO2017050264**

(87) Internationalt publikationsnr.: **WO2018070878**

(30) Prioritet: **2016-10-13 NO 20161640**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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(54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF METANOL OG/ELLER METAN**

(56) Fremdragne publikationer:
DE-A1- 4 332 789
DATABASE WPI Week 199701 Thomson Scientific, London, GB; AN 1997-011743 XP002777060, -& WO 96/36219 A1 (HITACHI METALS LTD) 21 November 1996 (1996-11-21)

DESCRIPTION

Ambit of the Invention

[0001] The present invention relates to a process for producing methanol and/or methane by using carbon dioxide sequestered from dissolved carbon dioxide in water taken or isolated from a land-based plant for raising or farming aquatic animals such as fish combined with hydrogen originating from electrolysis of water through the reactions (I) or (II)

$$CO_2 + 3H_2 => CH_3OH + H_2O \qquad (I)$$

$$CO_2 + 4\ H_2 => CH_4 + 2H_2O \qquad (II)$$

wherein the methanol/methane is created through the steps of

1. a) electrolysis of water for forming hydrogen gas and oxygen gas,
2. b) transferring the oxygen gas from step a) to a plant for breeding aquatic animals for oxygenating the water in said plant to be used for the animal's breathing of the water in said plant for forming CO_2 to be sequestered from said breeding water to be used in the reactions (I) or (II) supra, and
3. c) returning said sequestered carbon dioxide to a plant for conducting the reaction(s) (I) and/or (II) supra for creating methanol and/or methane by combining said carbon dioxide with the hydrogen originating from said electrolysis of water. Particularly the present invention is related to the use of carbon dioxide-rich water from a land-based breeding plant for aquatic animals, e.g. fish farms, for producing methanol and/or methane by combining said carbon dioxide with hydrogen originating from electrolysis of water and further optionally returning the by-product oxygen originating from said electrolysis of the water to the water in the breeding plant for said aquatic animals.

Background for the invention

[0002] Based on both environmental and economic considerations it is advantageous to use CO_2 being dissolved or stored in water. The combination of farming aquatic animals such as fish for creating carbon dioxide dissolved in the water from the fish farming plant, removing the carbon dioxide from the breeding water and combining this sequestered carbon dioxide with hydrogen for creating compounds for further exploitation, such as methanol and/or methane, will not only provide a sustainable living environment for the aquatic animals by removing said carbon dioxide, but will also provide a source for carbon dioxide to be used as starting materials for producing methane and/or methanol. The produced methanol/methane may be

further used for producing e.g. fish feed. A combination of fish breeding with the production of methanol/methane will improve both processes to be more environmentally friendly and sustainable.

Prior Art

[0003] The production of methanol through a reaction of carbon dioxide and hydrogen is known from WO 95/214123. Hydrogen gas and oxygen gas is produced through electrolysis of water. The oxygen gas is then introduced into a carbon-based process wherein CO_2 is produced as a waste gas. The CO_2 gas is subsequently isolated and transported to a methanol-generating unit. In this unit hydrogen gas is added and methanol is produced by a reaction between the hydrogen and the carbon dioxide. Instead of the CO_2 gas being treated as a waste product this is being used for producing methanol.

[0004] A process for producing methanol is also known from DE patent 4332789 through a reaction between carbon dioxide and hydrogen, wherein the hydrogen originates from the hydrolysis of water. A similar process is known from EP 2978732 B1 disclosing a method for producing methane wherein hydrogen originating from the hydrolysis of water is reacted with CO_2 in a reactor for producing methane.

[0005] For cultivating and breeding aquatic organisms it is generally known that CO_2 should be removed from the water and that the water should be added oxygen for sustaining the living conditions for the aquatic animals. This is e.g. disclosed in US 2013/0112151 A1. JP 2003259759 A discloses removing carbon dioxide from an aqua culture plant while supplying oxygen.

1a. Production of methanol

[0006] Based on a newly developed technology by "Carbon Recycling International" (CRI), 201 Kopavogur, Iceland (www.CR.I.IS) methanol may be produced in an industrial scale from CO_2 and H_2.

$$CO_2 + 3H_2 \Rightarrow CH_3OH + H_2O$$

[0007] When the hydrogen gas is produced through electrolysis of water or through natural gas by renewable energy such as by energy issued from solar panels, wind power plants/windmills or conventional water power plants, methanol as well as other products that may be produced based on methanol, may be said to be "green" or environmentally friendly

(i.e. without or with a small environmental load) and ranges from additives for fuels to glue in fiber wood as well as plastics in tools, toys, cars or accessories such as kitchen equipment, aids for the handicapped, rails, etc.

[0008] The electrolysis of water creates oxygen gas as well in an amount of about 8 kg oxygen per kilogram of hydrogen gas, as well as hot water from the cooling of the electrolysis plant, where both these items are wanted for a land-based plant for cultivating or breeding aquatic organisms such as in fish cultivation plants.

1b. Production of methane

[0009] Methane may be produced from CO_2 and H_2 via a Sabatier-reactor producing methane through the overall reaction

$$CO_2 + 4H_2 => CH_4 + 2H_2O$$

[0010] In this reaction it is additionally produced heat. The methane gas is fed into a recently developed fermenting reactor (developed by "Bioferm/Calysta") producing fish feed ("FeedKind"™ protein) as a replacement for fish meal being supplied to the fish.

[0011] The electrolysis of water forming oxygen and hydrogen, may be included in a closed circuit being connected to a conduit for supplying isolated CO_2 originating from the combustion of oxygen by fish through their metabolism (dissolved in the water or supplied externally) and carbon through the fish feed, wherein CO_2 dissolved in the water may be sequestered by using state of the art techniques such as membrane extraction, aeration through pressure reduction, by using ultrasound waves for forming CO_2 bubbles, etc.

[0012] The isolated carbon dioxide may be thus be connected to both the production of methanol and/or methane in a closed circuit whereon O_2 is formed by the electrolysis of water being transported in a closed circuit to a fish farming plant that subsequently produces carbon dioxide that may be used for producing methanol and/or methane as explained supra. The methane may subsequently be used as a raw material for the production of e.g. fish feed that may be fed back to the fish as well.

[0013] Thus the present invention concerns, in one embodiment, the use of CO_2 extracted/sequestered from water from an aqua-farming plant such as a land-based fish-farming plant for producing methanol/methane through adding hydrogen to said CO_2 and reacting said hydrogen with said carbon dioxide in agreement with the above reactions (I) and/or (II). The produced methanol/methane may be used as starting materials for further

production of articles. In one embodiment the sequestration of CO_2 may be accomplished by the water in the cultivation/breeding tank being circulated in a closed system to a unit liberating CO_2 from the water. It has not been found that capturing CO_2 from water originating from the cultivation of aqueous organisms has been suggested as a starting material for the production of methanol and/or methane or that this has been attempted before. The system provides a unique circular supply chain and it is self-sufficient, as detailed below, since the fish provide enough CO_2 to feed a methanol/methane and hydrolyzer plant that in turn will provide more oxygen as a bi-product than needed by the fish.

[0014] The expression "fish farming plant" or "plant for farming aquatic animals" should in the present context be interpreted to include the farming or breeding of other aquatic animals besides fish, e.g. crustaceans (crayfish, shrimp, crab) or mollusks (oysters, scallops, etc.). A fish farming plant may include a fresh water plant as well as a salt water plant provided they are closed systems and are not to any significant extent supplied with water from external sources. Such a combination of electrolysis of water and the production of CO_2 from aquatic animals will also qualify as a carbon-negative process with an advantageous effect on the climate and particularly the water quality in the fish breeding plant. The combined plants will produce fish with no or insignificant outlet to the environment and also bio-based methanol/methane, all provided the electric power used is taken from a renewable source.

[0015] It is well known to make bio-fuels like bio-ethanol from plants and trees, but it is also a well-known concern that demand for such fuels might lead to overtaxing of the bio-production capacity in nature and start competing with food production. In the case of the present invention, more demand for bio-fuel will stimulate more production of fish.

2. Fish farming in closed and land-based plants with return of water

[0016] In a closed system it is possible to obtain optimal growth and breeding conditions for the aquatic organisms/fish and additionally avoid serious diseases or environmental problems including diseases/fish diseases and the escaping of fish because the water is returned to the fish farming plant subsequent to purification/filtration/sedimentation/flotation and temperature adjustment. However, it is required a lot of O_2 to spruce up the water (the fish using oxygen dissolved in the water for their energy/metabolism while producing CO_2 through such metabolism). In a closed cultivation system it is also possible to cultivate other organisms such as crustaceans (crawfish etc.) and scallops (fresh water scallops) being organisms that require oxygen for their metabolism as well.

- The electrolysis plant will, through the electrolysis of water, provide the required H_2 to the methanol/methane production as well as O_2 together with hot water that may be used for:
    - more convenient extraction of CO_2 from the water in the fish farming ponds,
    - the treatment of sediments and waste and storage thereof to useful biomass,

- regulating the temperature in the raising and breeding ponds/tanks,
- supplying hot water for slaughtering the fish, sanitizing equipment, sanitary treatment of the fish meat, etc.

[0017] Hot water may in one embodiment also be used in heat exchanger for elevating the temperature of the water from the fish cultivation tank(s) for preparing removal of the entrained CO_2 therein. Cold water is known to assimilate gases such as O_2 and CO_2 better than hot water. E.g. water at a temperature of 60-90°C carries far less entrained gas than water at e.g. 4-15°C. Consequently the temperature in the fish cultivation and breeding tanks is maintained at temperatures that are suitable for the aquatic animals therein. CO_2-rich water from the cultivation/breeding tank(s) will in one embodiment consequently be heated after having been removed from the cultivation tank(s) but prior to the CO_2 removal step of the process according to the invention.

[0018] Extraction of CO_2 from water is known inter alia from "SFE Extraction and CO_2 Extraction" (www.waters.com).

- For each molecule of O_2 being used by the aqueous organisms/fish, said organisms/fish forms one molecule of CO_2, or per weight:
  - 1000 kg O_2 = > 1200 kg CO_2 giving a CO_2-factor of 1,2.

[0019] In a closed system carrying live aqueous organisms CO_2 has to be removed from the water for maintaining acceptable living conditions for the organisms such as acceptable pH-values (normally about pH 6 - 8, preferably about pH 7). CO_2 is normally associated with elevating the pH of water by forming carbonic acid ($CO_2 + H_2O => H_2CO_3$), and is considered to be a waste product with negative environmental consequences. Many of such negative consequences are dealt with in closed systems such as the system according to the present invention.

[0020] The present invention will become better understood with reference to the enclosed figure showing an embodiment of a system according to the present invention combining the formation of oxygen 2 and hydrogen 3 from electrolysis 1 of water wherein CO_2 is isolated 4,4' from the water taken from used water including entrained CO_2 from a cultivation/breeding tank/pond 5 for aquatic animals/fish. The isolated CO_2 is reacted with hydrogen originating from the electrolysis 1 of water forming methane and/or methanol 6,6' as explained supra. In one embodiment the methane may be supplied to a bacterial culture 8 as a growth substrate for creating protein to be used in e.g. fish feed. Such protein may in one embodiment constitute about 30% of protein included in such fish feed.

[0021] In an alternative embodiment methanol created by the process according to the invention may be used as a starting material for making more complex substances (e.g. plastics, oil, etc.) or may be used as a fuel or a fuel additive.

[0022] In one embodiment hot water used in the system according to the invention may be supplied from an external source or may be water recirculated from the cultivation/breeding tank 5. In an alternative the CO_2-poor water from the carbon dioxide-extracting section 4 may be supplied with oxygen 2 originating from the electrolysis section 1 of the system according to the invention and be returned in an oxygen-rich state back to the cultivation/breeding tank/pond 5. This is indicated by a dotted line 7 running from the carbon dioxide removal stage 4 to the supply line 2 carrying oxygen from the electrolysis stage 1 to the cultivation/breeding tank/pond 5.

[0023] The energy in the hot water from the electrolysis stage 1 may be heat-exchanged into cooling of the water in closed plants (not shown). Hot water (exceeding 80°C) being collected as a by-product from the production stages of methanol and methane 6,6', may be used for disinfection or directly for slaughtering fish, and may additionally and optionally be used for drying sludge collected from the cultivation/breeding tank/pond 5. Such sludge may in one embodiment be used as e.g. fertilizer.

[0024] In a closed cultivation system for aquatic animals/fish excess CO_2 should be removed from the water for maintaining acceptable pH values, and the CO_2 is also considered as a waste product with negative environmental effects such as e.g. acidification of the water through the formation of H_2CO_3 and HCO_3. A too high content of CO_2 in the water will also have as a consequence that it will become difficult for the aquatic animals to "breathe" (the water becomes CO_2-poisoned). Several other environmental consequences, e.g. the prevention and/or treatment of diseases and parasites (e.g. salmon lice), escape, no effect on the environment through medication, removal of waste (feces, dead animals, over-feeding, etc.) is easily taken care of in closed cultivation/breeding systems.

[0025] Regular feed or feed/protein produced from the bacterial fermentation of CH_4 in the fermentor 8 may be introduced into the fish farming tank/pond 5 through lines 9,9'.

[0026] 3. The addition of extra oxygen (O_2) to fish cultivation/breeding/farming plants has been recommended in studies performed by IRIS (previously Rogalands-forskning), but integration with a methanol or methane production plant is a new concept. The new concept is to capture CO_2 created by cultivated/bred organisms/fish and process this as a raw material in the methanol/methane plant. This idea is new probably because the technology for producing methanol, as disclosed supra, is rather new. The use of CO_2 in this way reduced the capital expenses with about 30% and the production costs with about 14% for the methanol production and free oxygen and heat assists in making land-based fish raising and breeding plants very profitable. By utilizing CO_2 for producing methane and fish feed about 30% of the expenses may be saved for necessary feed.

[0027] The liberated oxygen expelled from the electrolysis plant 1 may also be used for other purposes than the addition to a fish cultivation/breeding plant, e.g. for combustion systems/plants for garbage, from which further CO_2 may be introduced into the methanol/methane production plant 6,6' (not shown).

[0028] The balance for the methanol production related to fish farming/breeding (per 1000 kg methanol) is:

- produced O_2 from H_2O: 1541 kg
- 75% of O_2 introduced in the fish farming: 1157 kg
- CO_2 available from the fish: $1157 \cdot 1{,}2 = 1388$ kg
- CO_2 required for producing methanol: 1380 kg ≈ balance

[0029] Some extra oxygen may be provided to the fish because the fish may not be able to assimilate it all. The extra oxygen originating from the electrolysis covers this requirement.

[0030] The enclosed figure depicts a possible flow chart for a system for producing methanol/methane according to the invention, wherein said system includes an electrolysis section 1 producing hydrogen and oxygen from the cleaving of water molecules, and said system further including a closed cultivation/breeding container/pond 5 for aquatic organisms creating CO_2 to be liberated into the water surrounding said organisms forming CO_2-rich water, said CO_2-rich water being transported to a CO_2-liberating section forming gaseous CO_2 and CO_2-poor water, said liberated gaseous CO_2 being transported to a reactor 6,6' and being combined with said hydrogen from said electrolysis plant 1 for creating methanol and/or methane as an end product, said methanol/methane being isolated and exited from said system.

[0031] Technology for harvesting CO_2 from water in an industrial scale is available as explained supra, and the system according to the invention will, in one embodiment, capture the formed CO_2 as well and thereby avoid accumulation. If this security measure should fail, there exist methods for removing CO_2 from water without capturing the CO_2, e.g. like bubbling air through the water in an aquarium. The loops for transporting oxygen, hydrogen and carbon dioxide between a methanol/methane production plant and a plant for cultivating/breeding aquatic organisms/fish improve both to a large extent by:

1. 1. Reducing both capital and production expenses for the methanol/methane production.
2. 2. Providing a continuous supply of oxygen and energy to the fish raising/breeding plant.
3. 3. Replacing parts of the need for fish feed.

[0032] In summary the present invention may be presented by the following features:
The process according to the invention is conducted by producing methanol and/or methane by the reactions (I) and/or (II)

$$CO_2 + 3H_2 = > Z\ r\ CH_3OH + H_2O \qquad (I)$$

$$CO_2 + 4\ H_2 => CH_4 + 2H_2O \qquad (II)$$

wherein the methanol/methane is created through the steps

1. a) electrolysis of water for forming hydrogen gas and oxygen gas,
2. b) transferring the oxygen gas from step a) to a plant for breeding aquatic animals for oxygenating the water in said plant to be used for the animal's breathing of the water in said plant for forming CO_2 to be sequestered from said cultivation/breeding water to be used in the reactions (I) or (II) supra, and
3. c) returning said sequestered carbon dioxide to a plant for conducting the reaction(s) (I) and/or (II) supra for creating methanol and/or methane by combining said carbon dioxide with the hydrogen originating from said electrolysis of water.

[0033] Alternatively the invention may be viewed as using carbon dioxide-rich water originating from a cultivation plant/container/pond for aquatic animals/fish, after the liberation of said carbon dioxide from said cultivation/breeding water, to be combined with hydrogen originating from electrolysis of water for forming methanol and/or methane.

[0034] The aquatic animals such as fish that may be cultivated/bred in a closed cultivation/breeding plant comprises fish types such as e.g. carp, mullet, bass, abbor, pike, trout, etc. The water used for cultivating/breeding the aquatic animals may be salt or fresh, fresh water being preferred. Organisms thriving in fresh water other than fish, and that may be cultivated in a land-based closed cultivation/breeding plant either alone or together with the different fish types, may be fresh water crawfish, fresh water clams, pearl fresh water oysters, etc.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO95214123A [0003]
- DE4332789 [0004]
- EP2978732B1 [0004]
- US20130112151A1 [0005]
- JP2003259759A [0005]

Patentkrav

1. System til fremstilling af metanol/metan, hvilket system omfatter et elektrolyseafsnit (1) der producerer hydrogen og oxygen fra spaltningen af vandmolekyler, og hvor nævnte system yderligere omfatter en lukket dyrknings-/formeringsbeholder/-dam (5) til vandorganismer der skaber CO_2 via stofskiftet af vanddyrene samt bionedbrydning af fæces og ubrugt foder ved bunden af formerings-/dyrkningsbeholderen/-dammen, som skal frigøres til vandet der omgiver nævnte organismer, som danner CO_2-rigt vand, hvor nævnte CO_2-rige vand transporteres til et CO_2-friørende afsnit der danner gasformigt CO_2 og CO_2-fattigt vand, hvor nævnte frigjorte gasformige CO_2 transporteres til en reaktor (6,6') og kombineres med nævnte hydrogen fra nævnte elektrolyseanlæg (1) for at skabe metanol og/eller metan som et slutprodukt, hvor nævnte metanol/metan isoleres og udledes fra nævnte system, hvor systemet er **kendetegnet ved, at** oxygenet frigjort fra nævnte spaltning af vandmolekyler introduceres til vandet i dyrknings-/formeringsanlægget for vanddyrene.

2. System ifølge krav 1, hvor nævnte oxygen tilsættes til det CO_2-fattige vand stammende fra nævnte CO_2-friørende afsnit (7) forud for dets genindførelse til dyrknings-/formeringsanlægget (5).

3. Fremgangsmåde til fremstilling af metanol/metan ved anvendelsen af et system ifølge et hvilket som helst af kravene 1-2, hvor metanolen og/eller metanen dannes igennem de overordnede reaktioner

$$CO_2 + 3H_2 => CH_3OH + H_2O \qquad (I)$$

$$CO_2 + 4\ H_2 => CH_4 + 2H_2O \qquad (II)$$

hvor metanolen/metanen skabes via trinnene

a) elektrolyse af vand til dannelse af hydrogengas og oxygengas,

b) isolering af CO_2 fra det CO_2-rige vand stammende fra dyrets ånding af vandet i nævnte anlæg til dannelse af CO_2 som skal udskilles fra nævnte formeringsvand for at blive anvendt i reaktionerne (I) eller (II) supra, og

c) returnering af nævnte udskilte kuldioxid til et anlæg til at udføre reaktionen(-erne) (I) og/eller (II) supra for at skabe metanol og/eller metan ved at kombinere nævnte kuldioxid med hydrogenet stammende fra nævnte elektrolyse af vand, hvilken fremgangsmåde er

kendetegnet ved, at oxygenet frigjort fra elektrolysen af vandet introduceres i vandet i dyrknings-/formeringsanlægget for vanddyrene (5).

4. Fremgangsmåden ifølge krav 3, hvor kuldioxidrigt vand fra et landbaseret formeringsanlæg for vanddyr, eksempelvis fiskefarme, anvendes til fremstilling af metanol og/eller metan ved at kombinere nævnte kuldioxid med hydrogen stammende fra elektrolyse af vand og returnering af oxygenet stammende fra nævnte elektrolyse af vandet til vandet i formeringsanlægget for nævnte vanddyr.

5. Fremgangsmåden ifølge et hvilket som helst af kravene 3 eller 4, hvor nævnte dyrknings-/formeringsanlæg (5) er et lukket fiskeopdrætsanlæg, hvor vandet recirkuleres efter at være blevet frigjort for CO_2.

6. Fremgangsmåden ifølge et hvilket som helst af kravene 3 til 5, hvor varmt vand stammende fra elektrolysen af vand forsynes til dyrknings-/formeringsanlægget for at blive anvendt i desinfektion eller slagtning af spiselige vanddyr og/eller styring af temperaturen i formerings-/dyrkningsbeholderen/-dammen.

7. Fremgangsmåden ifølge et hvilket som helst af kravene 3 til 6, hvor vanddyrene er fisk der kan opdrættes i et landbaseret dyrknings-/formeringsanlæg, såsom karpe, multe, bars, gedde, ørred osv. eller hvor nævnte vanddyr er forskellige fra fisk såsom ferskvandskrebs, ferskvandsperlemuslinger, ferskvandskammuslinger, osv.

8. Anvendelsen af CO_2-rigt vand stammende fra et anlæg til dyrkning/formering af vandorganismer for isolering af CO_2 der skal reageres med hydrogen stammende fra elektrolysen af vand til dannelse af metanol og/eller metan i en fremgangsmåde ifølge krav 3.

9. Fremgangsmåden ifølge et hvilket som helst af kravene 3 til 7 eller anvendelsen ifølge krav 8 yderligere anvendende den producerede metan til fremstilling af fiskefoder.

DRAWINGS