



(51) International Patent Classification:

C12M 1/00 (2006.01) C12P 7/08 (2006.01)

(21) International Application Number:

PCT/IB2020/051538

(22) International Filing Date:

24 February 2020 (24.02.2020)

(25) Filing Language:

Italian

(26) Publication Language:

English

(30) Priority Data:

102019000002763 26 February 2019 (26.02.2019) IT

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: OXIDATION AND GASIFICATION METHOD AND SYSTEM PRODUCING BIOETHANOL

(57) Abstract: The present invention relates to a method and a system for producing bioethanol, which combines the processes of oxidation and gasification of lignocellulosic material.



DESCRIPTION**"OXIDATION AND GASIFICATION METHOD AND SYSTEM FOR
PRODUCING BIOETHANOL"**Technical field of the invention

The present invention finds application in the bioethanol production field.

Background art

5 First and second generation systems for producing ethanol are known.

A conventional first generation system (1G) for producing ethanol starting from sugar cane for transportation is diagrammatically shown in Figure 1.

10 This comprises a sugar extraction section (100), a sugar juice treatment and condensation section (300), a fermentation section (400), a distillation section (500) and a dehydration section (600).

15 More specifically, the sugar cane is cut into pieces, defibered by means of a shredder and the sugar is extracted by means of a series of mills or by means of a diffuser.

From this section two products are obtained: one is the sugar juice destined to produce ethanol and the
20 other is the bagasse, the solid residue, which is generally employed as fuel to generate steam used to

meet the requirements of the plant and also to produce electricity by means of a steam turbine.

The electricity thus produced is used, in turn, to meet the needs of the plant and any possible surplus
5 is fed into the national or local grid.

With regard to the bagasse, before being burnt, it is subjected to a treatment so as to reduce its moisture content by up to 50%-55%, both for combustion efficiency and to reduce emissions.

10 This reduction in residual moisture, which may be achieved by means of mills, however, entails a substantial energy consumption and requires equipment which is anything but negligible in size (dewatering section).

15 The boiler further comprises a combustion fume treatment section so as to comply with the increasingly stringent limits on emissions.

The bagasse may also be sent, partially or totally, to a second generation ethanol system (2G) where it is
20 converted to ethanol by means of enzymatic hydrolysis and subsequent fermentation.

The solid residue of a 2G system (second generation) is lignin, which, generally, is burnt to produce steam and electricity.

From the distillation section (500) there are obtained hydrate alcohol, which must be subjected to subsequent dehydration (600) so as to be used as transportation fuel to be mixed with petrol, and an
5 aqueous stream, rich in residual organic compounds and dissolved salts which takes the name of "vinasse" (stillage).

The vinasse may be subjected to condensation to reduce the volume thereof, sent, as such, to an
10 evaporation tank, used to irrigate the sugar cane fields, or sent to a treatment plant.

It should be noted that, for each liter of alcohol, up to 12-14 liters of vinasse may be produced.

The condensation of the vinasse is a process that
15 requires a substantial energy consumption; the use, as such, as fertilizer is now prohibited in many countries, and it also causes the enrichment of salts in the fields close to the facility, which negatively affects the productivity of sugar cane.

20 An alternative manner to dispose of the vinasse, for which some technologies are already commercially available, is to condense it and to spray it in the boiler that burns the bagasse.

Therefore, more and more often, the disposal in a
25 dedicated treatment plant is required, which, however,

is somewhat complex, requires large volumes (and therefore space in the plant), and, above all, the cost of a Waste Water Treatment Plant conceived for achieving a zero liquid discharge condition (ZLD) is
5 comparable to that of the ethanol production line.

On the other hand, the treatment plant with a crystallization unit attached so as to recycle the water for the ethanol production process is complex and expensive.

10 While a first generation system (1G) for producing ethanol may be fed with any biomass containing fermentable sugars or starch (for example, sugar cane, corn, sugar beet, sugar sorghum, etc.), a second generation process system (2G) may be fed with
15 different lignocellulosic materials (for example, bagasse, corn stover, wheat straw, rice straw, forest residues, etc.).

The gasification process in supercritical water

Gasification in supercritical water is a recent
20 technology, which allows the conversion of waste water containing organic compounds into fuels with a high hydrogen and light hydrocarbon content.

The treatment of organic compounds is carried out under temperature and pressure conditions at which the

water is in supercritical conditions (temperatures above 374°C and pressure greater than 221 bar).

Under these conditions, water behaves as a non-polar fluid and is capable of solubilizing organic matter and of breaking the molecules thereof.

Usually, the process is operated at temperatures between 400°C and 650°C and with pressures between 250 bar and 350 bar, and has interesting conversion efficiencies, especially for wet biomass.

The high solubility of the reaction intermediates limits the formation of "tar" (a liquid rich in aromatic hydrocarbons of the tar type, carbon dioxide and nanoparticulate, harmful to plant) and "char" (a carbonaceous solid very similar to coal), which are among the main drawbacks of conventional gasification.

Gasification in supercritical water is an alternative, in addition to classic gasification, also to anaerobic digestion, with which it shares the advantage of not requiring a reduction of feedstock moisture, but which also has the advantage of requiring much shorter residence times, in the order of a few minutes.

Summary of the invention

The inventors of the present patent application have surprisingly found that it is possible to solve

the problem of the disposal of the vinasse and at the same time eliminate the dewatering section of the bagasse by means of a combined gasification (SCWG) and oxidation (SCWO) process in supercritical water.

5 Object of the invention

It is a first object of the invention a process for producing bioethanol, which uses an oxidation step and a gasification step in supercritical water.

In a second object, an plant is described for
10 carrying out the process of the invention.

Brief description of the Figures

Figure 1 shows the diagram of a conventional process for producing bioethanol in first generation systems;

15 Figure 2 shows a first and second generation integrated system for producing bioethanol;

Figure 3 shows the diagram of a system according to the present invention.

Detailed description of the invention

20 In accordance with a first object of the invention, it is described a process for producing bioethanol starting from sugar cane biomass.

In particular, such process comprises the following steps:

25 a) sugar extraction,

- b) evaporation;
- c) fermentation,
- d) distillation,
- e) alcohol dehydration.

5 The steps listed above are carried out according to the known art for first generation systems for producing bioethanol.

 Bagasse is obtained from the sugar (sucrose) extraction step a).

10 Vinsasse (or stillage) is obtained from the distillation step d).

 With regard to the extraction step a), this may be carried out by means of a first defibration step by means of a shredder, followed by an upstream solid
15 liquid extraction step inside a diffuser; alternatively, the extraction may be obtained with a series of mills.

 Thereby, from the sugar cane, a solid residue is also obtained, which is the bagasse, i.e. a
20 lignocellulosic residue characterized, when exiting a diffuser, by high moisture levels (even 85% of water).

 With regard to the distillation step d), as described above, it allows to obtain ethanol hydrate and, as a waste sub-product, the "vinsasse", which is a
25 liquid stream rich in organic fraction, characterized

by a Chemical Oxygen Demand (COD) of up to 30,000 and rich in dissolved and suspended salts.

For the objects of the present invention, the process for producing bioethanol comprises an oxidation
5 step.

In particular, such oxidation is carried out on the bagasse obtained from the extraction step a).

To this end, however, the bagasse is subjected to a pre-treatment step.

10 Said pre-treatment comprises, in particular:

- a thermal pre-treatment, and/or
- a chemical pre-treatment.

By means of the chemical pre-treatment, chemical agents (for example, sulfuric acid) and/or steam are
15 used to separate lignin by means of a process known as acid hydrolysis.

By means of the thermal pre-treatment, the bagasse is subjected to pyrolysis; in particular, such pyrolysis is carried out at a temperature of 400-600°C.

20 In particular, at least the following sub-products are obtained from the bagasse pre-treatment step:

- a gaseous sub-product,
- a solid sub-product,
- a liquid sub-product,

of which the solid sub-product is subjected to the oxidation step, described below.

With regard to the gaseous sub-product, this may be partially or totally used as fuel for the pre-treatment step itself.

For the purposes of the present invention, however, the liquid sub-product is sent to a gasification step, which will be detailed below in the present description.

Before being sent to the oxidation step, the solid sub-product obtained from pre-treatment step of the bagasse may be treated with a flow of water to increase its water content and thus render it more easily pumpable.

In fact, for being sent to the oxidation step, the slurry thus obtained is preferably pumped at a pressure of about 200-250 bar and more preferably of about 240 bar.

To this end, water or any liquid stream containing an organic load, such as, for example, sanitary waste water, may be used.

Such mixture will have an organic material mass content of about 5-25% (weight).

As described above, said mixture is sent to the oxidation step.

In one aspect of the invention, said mixture may also be sent to the gasification step.

According to the present invention, the oxidation step is carried out with water.

5 Since, for the purposes of the present invention, the oxidation step is carried out at a pressure of about 225-350 bar and at a temperature of about 700-1000°C, such step involves the use of water in supercritical conditions.

10 According to a preferred aspect of the invention, an oxidizing agent, which may be air or oxygen, is used in the oxidation step.

At least the following products are obtained from the oxidation step:

- 15 - steam,
 - fumes, and
 - water.

Heat is also obtained from the oxidation step, which may be used to generate steam.

20 In one aspect of the invention, steam is used to produce electricity and for meeting the needs of the plant; to this end, a steam turbine, connected to an appropriate current generator, is used.

The fumes resulting from the process, following an appropriate treatment, may be released into the atmosphere.

For example, they may be subjected to a washing
5 step, in an appropriate scrubber, after an appropriate cooling step; alternatively, they may be recovered as a stream rich in carbon dioxide, especially if oxygen or enriched air are used as an oxidizing agent.

The water possibly recovered from the washing step
10 may be sent to the gasification step mentioned above.

According to the present invention, the gasification step is carried out with water.

Since, for the purposes of the present invention, the gasification step, to which the liquid sub-product
15 obtained from the pre-treatment of the bagasse is subjected, is carried out at a pressure of about 225-350 bar and at a temperature of about 400-700°C, such step involves the use of water in supercritical conditions.

20 In one aspect of the invention, the heat or part of the heat produced during the oxidation step may be used in the process of the present invention and, in a preferred aspect, also in the gasification step mentioned above.

As described above, the liquid sub-product of the pre-treatment step is sent to a gasification step.

The following are obtained from the gasification step:

- 5 - a gaseous flow, represented by syngas, and
- a liquid residue, after cooling.

With regard to the liquid product consisting of the gasification sub-products, in a preferred aspect of the invention, this is sent to the oxidation step,
10 to be completely oxidized.

With regard to the gaseous flow, however, this mainly consists of hydrogen, methane, carbon dioxide and carbon monoxide.

The syngas is subsequently destined for a step of
15 desulfurization and to a partial or total removal of carbon dioxide.

Syngas as such may be used for producing methane, after an appropriate methanation step, or other products: methanol, synthetic fuels by means of Fisher-
20 Tropsh, ammonia, urea (also using CO₂ from the fermentation) or to increase the production of ethanol.

As described above, from the distillation step d), vinasse (or stillage) is obtained as the column bottom product.

For the purposes of the present invention, the vinasse is sent to the gasification step described above.

To this end, the vinasse is subjected to a
5 chemical, and possibly also thermal, pre-treatment step.

With regard to the chemical pre-treatment, this comprises a chemical neutralization step.

If necessary, a thermal pre-treatment of the
10 vinasse may be carried for concentration, to improve the processability and to recover water.

In particular, the vinasse is concentrated up to 15%-60%.

From such pre-treatment a product is obtained, to
15 which we can refer as treated vinasse (or treated stillage).

Furthermore, a purge product may be obtained, which is eliminated after appropriate treatment.

For the purposes of the present invention, the
20 treated vinasse (or treated stillage) is sent to the gasification step.

In a particularly preferred aspect of the present invention, the treated vinasse, or a portion thereof, may be mixed with the solid residue obtained from the
25 bagasse pre-treatment step, forming a slurry which is

sent to the oxidation step and/or to the gasification step.

According to another aspect of the invention (not shown in the Figures), the treated vinasse, or a
5 portion thereof, may be joined to the non-treated bagasse, i.e., without this having been previously subjected to any thermal pre-treatment, or having been subjected only to a mechanical treatment, forming a slurry, which is sent to the gasification step.

10 Such aspect may be carried out on a portion of the bagasse obtained from the extraction step.

The ratio between the (mass) flow of slurry sent to the oxidation step and the total liquid flow sent to the gasification step is between 0.5-2; if it is
15 close to or greater than two, the process allows the production of a surplus of thermal or electric energy, which may be exported.

In a preferred aspect of the present invention, the oxidation and gasification steps are both carried
20 out by using water in supercritical conditions.

In this regard, it is possible to carry out a direct heat transfer between the two steps by means of the flow of water coming from the oxidation step and sent to the gasification step.

In an alternative aspect of the invention, however, the heat transfer is indirect and occurs by means of the use of an intermediate fluid (for example, water in supercritical conditions) or through a
5 surface.

Therefore, for the purposes of the present patent application, the oxidation and gasification steps are integrated with each other, at least from the thermal point of view, and it is possible, more generally, to
10 refers to as an oxidation-gasification process, to which one or more of the sub-products of the ethanol preparation process are subjected.

In accordance with a second object of the invention, a system is described for carrying out the
15 process described above.

In particular, such system comprises:

- a sugar extraction section,
- an evaporation section,
- a fermentation section,
- 20 - a distillation section,
- an alcohol dehydration section,
- possibly, a pre-treatment section for the vinasse,
- possibly, a pre-treatment section for the bagasse,
- and
- 25 - an oxidation section and a gasification section.

According to a preferred aspect of the invention, the plant comprises both a vinasse pre-treatment section and a gasification section.

According to another preferred aspect, the
5 oxidation section and the gasification section are integrated with each other, at least from the thermal point of view.

In a particular aspect, in the system of the present invention, the vinasse pre-treatment section
10 is functionally connected to the gasification section.

This means that the products obtained from the thermal and/or chemical pre-treatment step of the vinasse may be sent directly to the gasification section.

15 In another particular aspect, in the system of the present invention, the bagasse pre-treatment section is functionally connected to the oxidation and gasification sections.

This means that the sub-products obtained from the
20 chemical and possibly also thermal bagasse pre-treatment step may be sent directly to the oxidation and gasification sections.

For the purposes of the present invention, as mentioned above, the oxidation section and the
25 gasification section are integrated with each other.

This means that one or more of the products obtained from one section may be sent to the other section.

For example, the water obtained from the oxidation
5 section may be sent to the gasification section.

Alternatively or in addition, the liquid products obtained from the gasification step may be sent to the oxidation section.

In any case, the two sections are thermally
10 integrated, since part of the heat developed in the oxidation section is sent to the gasification step.

As described above, gasification and oxidation steps with water, in particular, with water in supercritical conditions, are carried out respectively
15 in the gasification section and in the oxidation section.

From the above description of the present invention, the advantages offered by the present invention will be immediately known to the person
20 skilled in the art.

First of all, the process described may be implemented on existing systems, by making the necessary modifications.

Furthermore, by offering an alternative to the vinasse disposal by dispersion in the fields, it is

certainly desirable from an environmental point of view.

Similarly, it is favorable the fact that the water recovered downstream the process is free of pollutants and may be recycled in the process.

From the system engineering point of view, the advantages are several.

In fact, the use of the vinasse in a gasification step allows the disposal thereof, eliminating the need for a water treatment plant and the related process (waste water treatment).

On the other hand, the use of the bagasse, after an appropriate treatment, in an oxidation section, allows to eliminate a dewatering section, since the residual water is not a critical issue for the oxidation in supercritical water.

The gaseous discharge of the oxidation only requires a mild treatment, since a dedicated section for their treatment is not required.

Obtaining products such as syngas allows the further production of ethanol, methane, synthetic fuel by means of FT synthesis, ammonia and urea (also using fermentation CO₂).

CLAIMS:

1. A process for producing bioethanol starting from sugar cane comprising the steps of:
 - a) sugar extraction, obtaining the bagasse;
 - b) evaporation;
 - c) fermentation;
 - d) distillation, obtaining the vinasse;
 - 5 e) alcohol dehydration,wherein said bagasse and said vinasse are subjected to an oxidation-gasification process comprising an oxidation step and a gasification step, both carried out with water in supercritical conditions.
- 10 2. A process according to the preceding claim, wherein, before said oxidation-gasification process, said bagasse and/or said vinasse are subjected to a pre-treatment step.
3. A process according to the preceding claim, wherein
15 said bagasse is subjected to a thermal pre-treatment step, obtaining a gaseous sub-product, a liquid sub-product and a solid sub-product.
4. A process according to the preceding claim, wherein said liquid sub-product is subjected to the
20 gasification step.
5. A process according to any one of the preceding claims 2 to 4, wherein said vinasse is subjected to a

thermal and/or chemical pre-treatment step, obtaining a treated vinasse.

6. A process according to the preceding claim, wherein said treated vinasse is subjected to the gasification
5 step.

7. A process according to any one of claims 3 to 6, wherein said solid sub-product is subjected to the oxidation step.

8. A process according to the preceding claim, wherein,
10 before said oxidation step, said solid sub-product is mixed with a flow of water and/or with a portion of the treated vinasse.

9. A process according to any one of the preceding claims 2 to 8, wherein said treated vinasse is
15 subjected to the gasification step after being mixed with the non-treated bagasse or a portion thereof.

10. A process according to any one of the preceding claims, wherein said oxidation step and said gasification step are mutually thermally integrated,
20 directly or by means of an intermediate fluid.

11. A plant for the production of bioethanol starting from sugar cane, comprising:
- a sugar extraction section,
- an evaporation section,
25 - a fermentation section,

- a distillation section,
- an alcohol dehydration section,
- possibly, a pre-treatment section for the vinasse,
- possibly, a pre-treatment section for the bagasse,

5 and

- an oxidation section and a gasification section,

wherein said oxidation section and said gasification
section are mutually thermally integrated.

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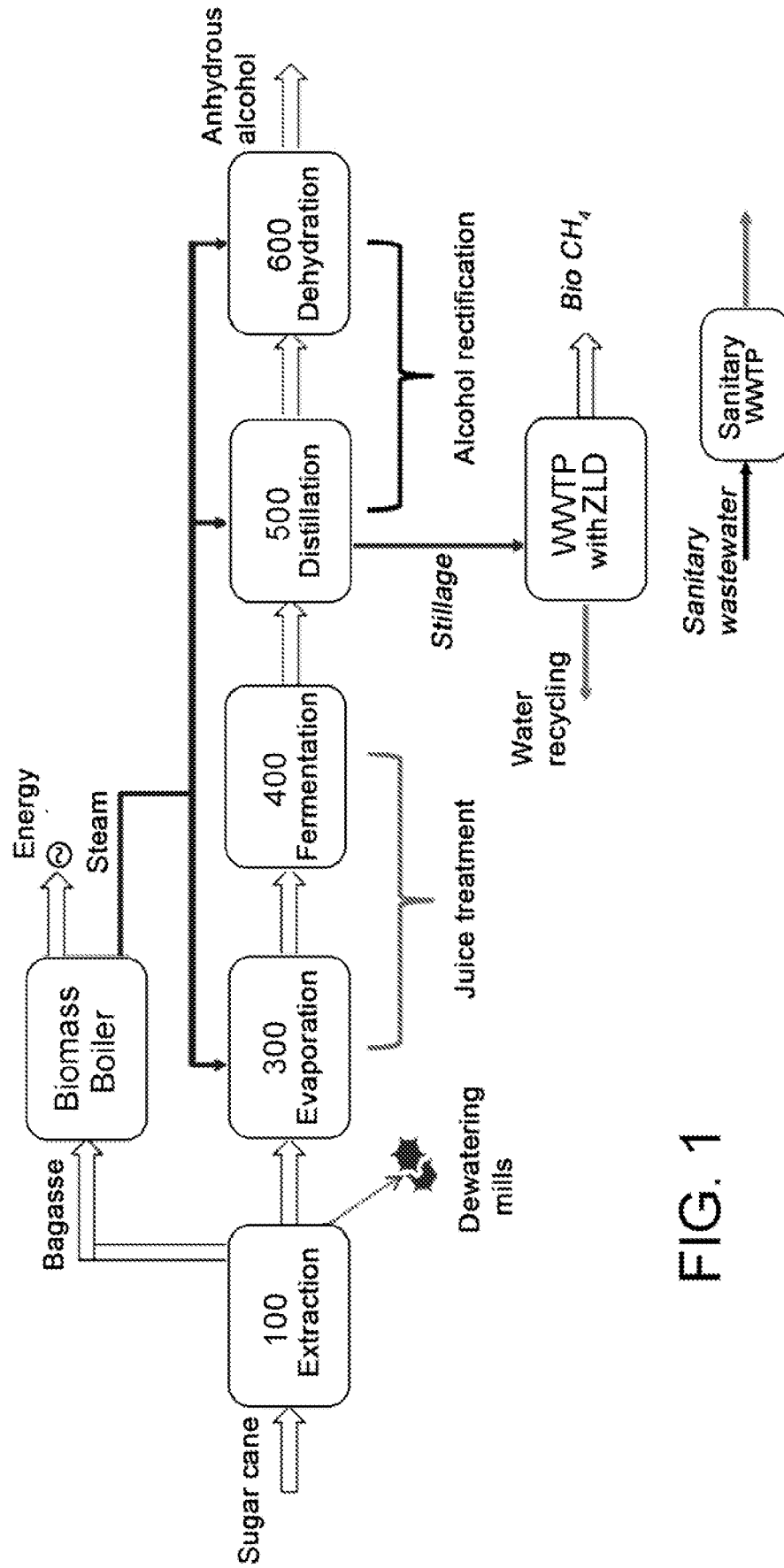


FIG. 1

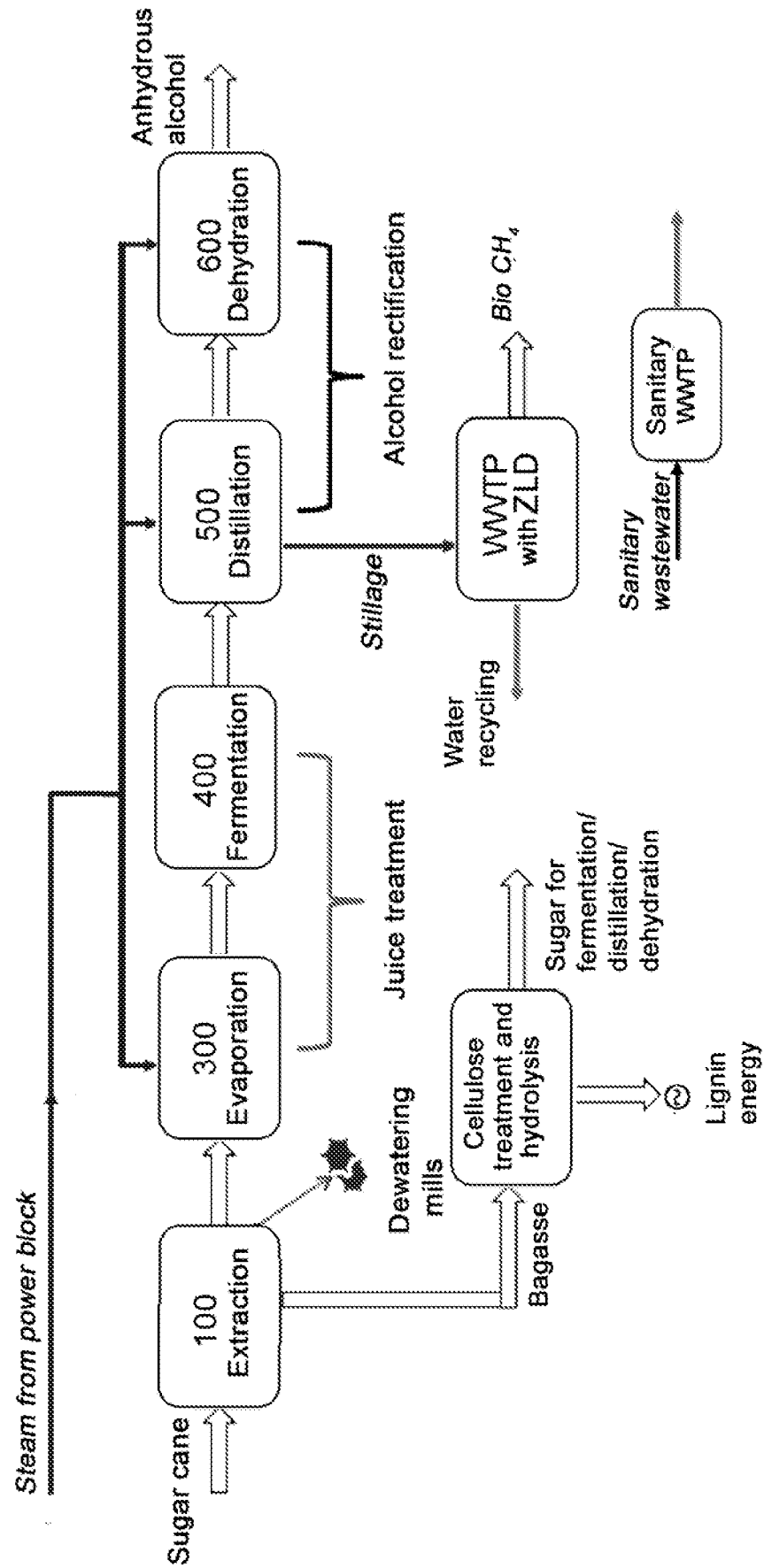
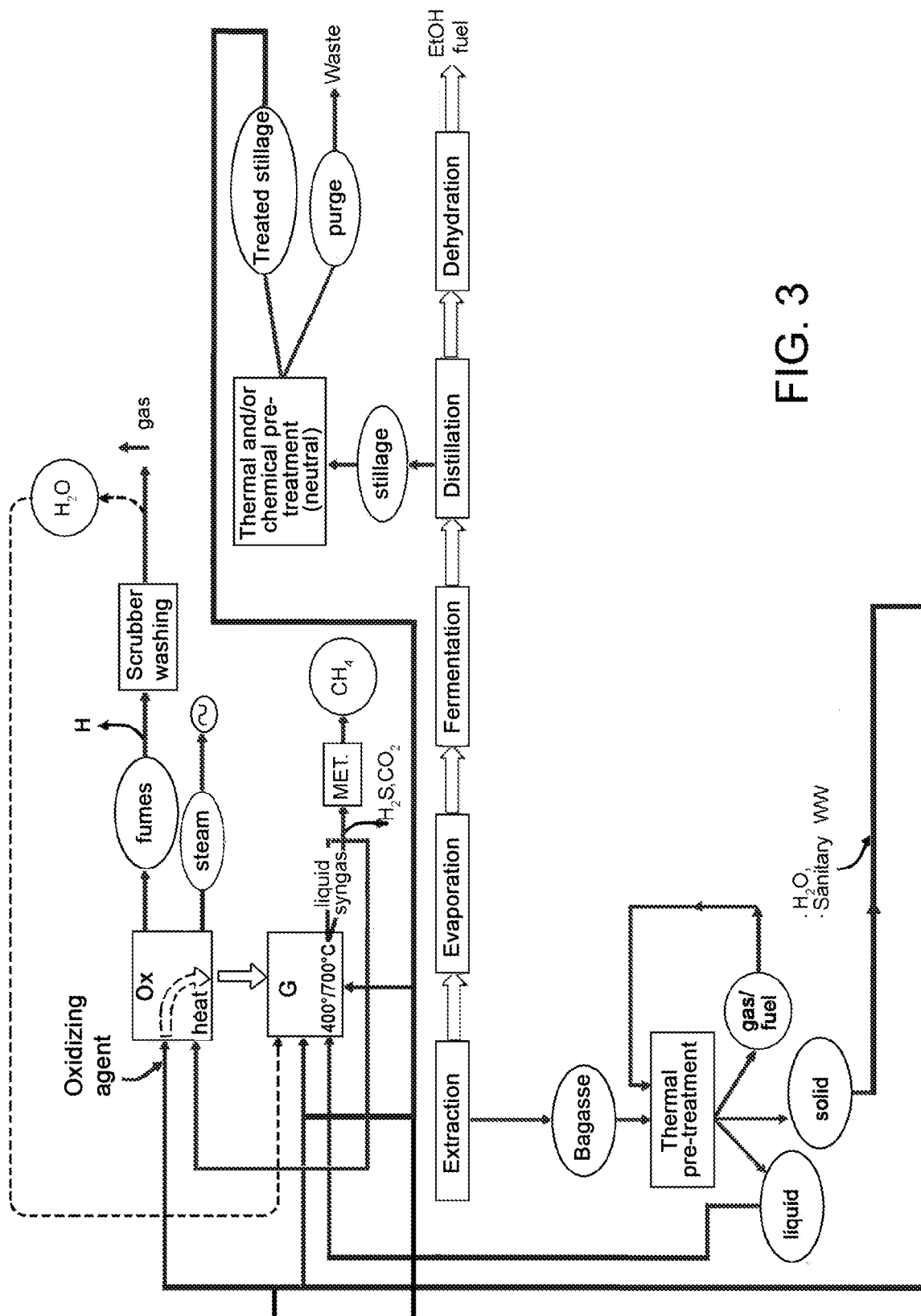


FIG. 2



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INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2020/051538

A. CLASSIFICATION OF SUBJECT MATTER
INV. C12M1/00 C12P7/08
ADD.

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)
C12M C12P

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)

EPO-Internal, BIOSIS, COMPENDEX, EMBASE, 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	ALBARELLI JULIANA Q ET AL: "Valorization of sugarcane biorefinery residues using supercritical water gasification: A case study and perspectives", THE JOURNAL OF SUPERCRITICAL FLUIDS, ELSEVIER, AMSTERDAM, NL, vol. 96, 16 September 2014 (2014-09-16), pages 133-143, XP029112105, ISSN: 0896-8446, DOI: 10.1016/J.SUPFLU.2014.09.009 point 2.1.3; abstract; figure 1	1-11
A	WO 2011/000831 A2 (GEA WIEGAND GMBH [DE]; SCHORMUELLER MATTHIAS [DE]) 6 January 2011 (2011-01-06) page 3, line 6 - page 8, line 24; figures 1-3	1-11
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☒ 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

17 June 2020

Date of mailing of the international search report

25/06/2020

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2020/051538

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 2016/166650 A1 (ARCHIMEDE S R L [IT]) 20 October 2016 (2016-10-20) page 5, line 17 - page 6, line 29 -----	1-11
A	WO 2011/063484 A1 (CT DE TECNOLOGIA CANAVIEIRA CTC [BR] ET AL.) 3 June 2011 (2011-06-03) -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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